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No. 127. Vol. 20.

REPORTS ON THE PROGRESS OF NAPHTHOLOGY, 1933.

The Cracking Art in 1933.*

By GUSTAV EGLOFF, Ph.D., M.A., M.Am.Inst.Chem.E., M.Am.Chem.Soc. (Member), and BADONA L. LEVINSON.

I. INTRODUCTION.

The advance of the cracking art in 1933 has been marked in many directions. The tendency has been more and more toward careful fundamental research into the basic factors involved in the cracking reaction in order to improve operating results. Cracked products are being evaluated to an ever-increasing extent according to quality rather than quantity, *e.g.*, higher octane value rather than yield of gasoline. For that reason the ratio of cracked to straight-run motor fuel steadily increases, in the United States and in foreign countries as well.

National policies in numerous countries are aiding the expansion of cracking facilities by fostering their own refining industries and discouraging importation of finished products.

It is increasingly notable that the modern refinery tends to centre about the cracking unit as its most vital part. Moreover, there is a greater realisation of the outstanding need for suitable materials to build equipment which will withstand the increasingly severe operating conditions of cracking. Materials for high pressure, high temperature equipment are being constantly studied and developed.

A noteworthy tendency in commercial cracking plants is directed toward multiple coil cracking, so that each fraction of the charge is treated under its own optimum conditions.

So-called by-products of the cracking process have increased in number and importance to such an extent that cracking conditions are sometimes regulated to produce other products than gasoline. Alcohols from cracked gases and gasoline, and asphalts from cracked residues are outstanding examples.

Cracking capacities of plants in the United States in August, 1933, according to the Western Petroleum Refiners' Association report,[1] and the *Oil and Gas Journal* survey,[2] amounted to

* This report covers publications from November 1, 1932, to December 1, 1933.

[1] *Statistical Bulletin*, 158.

[2] *Oil & Gas J.*, 1933, **31** (45), 40. The figure reported in the *Oil & Gas J.* survey for 1933 was based on raw stock only, and would be equivalent to the figure quoted here if based on both raw and rerun stocks as in former years.

2,044,645 barrels daily, an increase of 90,000 barrels over the daily capacity of 1,954,550 barrels in 1932. Foster,[3] surveying refineries in the Mid-Continent region, reports cracking in 63 refineries with estimated capacities of 320,000 barrels daily.

Manufacture of cracked gasoline in the United States[4] for the first eleven months of 1933 amounted to 166,384,000 barrels, as compared with 157,219,000 barrels in the corresponding period of 1932. For the same period, the amount of straight-run gasoline and of benzole increased in 1933 over 1932, while natural gasoline decreased. The barrels of each kind of motor fuel produced and the percentage of increase or decrease are shown in the table :—

Motor Fuel Produced. Period, January to November Inclusive.
(Figures denote 1000 barrels of 42 gallons.)

	1932.	1933.	Per cent. increase.
Straight-run gasoline	180,074	180,736	0·36
Cracked gasoline	157,219	166,384	5·83
Natural gasoline	39,716	27,516	—7·40
Benzole	945	1,344	42·22

It is interesting to note that the increase in straight-run gasoline for the year amounted to less than 0·5 per cent., whereas cracked gasoline increased almost 6 per cent. over the 1932 quantity. Cracked gasoline, related to the total gasoline obtained from crude petroleum in 1933, was 47·9 per cent. (the remainder being straight-run gasoline), representing a considerable increase over 1932, when it was 46·1 per cent. Based on total gasoline production, including natural gasoline and benzole, cracked gasoline in 1933 represented 44 per cent., while straight-run was 47·8 per cent. The corresponding percentages for 1932 were 42·7 and 48·9 per cent. respectively. The year 1933, then, marks an increase for cracked gasoline corresponding to a similar decrease in straight-run gasoline. This may be explained, for the most part, by the cracking of straight-run gasoline into a high anti-knock fuel. Ziegenhain[5] especially notes the changing market in which straight-run gasoline is rapidly giving way to the cracked product.

Some exceptionally interesting trends in the relation between cracked and straight-run gasoline are to be noted in 1933. During the month of November the amount of cracked gasoline produced actually exceeded the straight-run—15,393,000 barrels to 14,798,000 barrels—so that straight-run gasoline represented only 45 per cent. of the total gasoline output for the month, while cracked gasoline was 46·8 per cent. Monthly figures in 1933 on cracking stock

[3] *Nat. Petr. News*, 1933, **25** (20), 111.
[4] Information Circular 6728, U.S. Bureau of Mines.
[5] *Oil & Gas J.*, 1933, **31** (40), 11.

charged to stills, cracked gasoline produced and cracked fuel oil obtained are listed in the table :—

	Cracking stock to stills. (1000 brls.)	Cracked gasoline. (1000 brls.)	Cracked fuel oil. (1000 brls.)
January	30,494	13,128	11,215
February	29,473	12,211	10,436
March	32,246	13,644	10,830
April	33,211	14,258	11,079
May	37,785	16,400	12,466
June	36,316	15,855	12,039
July	39,319	17,012	14,596
August	37,670	16,478	14,528
September	36,784	16,004	13,981
October	36,929	16,001	14,475
November	34,825	15,393	13,245

The increased utilisation of cracked gasoline, accompanied by a decreased use of the straight-run product, has been noted[6] to be curtailing crude oil demand. The reason offered is that since fuel oil cannot be marketed profitably itself in comparison with returns available from cracking, the trend is to crack further, at the expense of crude oil throughput.

Ziegenhain[7] has pointed out the continued trend in 1933 toward higher octane number motor fuel. Cracking, he indicates, is especially important in satisfying this quality demand, and continues to aid in raising the average octane number of gasolines on the market. Ziegenhain[8] also reports that this average octane rating has increased from 65 in 1932 to 69 in 1933. Divided into the individual grades of gasoline, the rise has been from 74 to 76 for premium grade, from 61 to 65 for regular grade, and 51 to 53 for third grade gasoline.[9] Coincident with this sharp increase, and made possible by it, is the continued increase in compression ratios of new automobiles. The average ratio has increased from 4·96 in 1931 to 5·50 in 1932, 5·59 in 1933 and 6·1 in 1934 models. These averages are claimed to represent about 90 per cent. of the cars sold during each year.

Increased octane number has been accompanied by increasing volatility and vapour pressure in 1933 motor fuels. Ziegenhain[9] remarks that revision of existing cracking units to meet these new requirements is only a temporary solution, and will mean eventual replacement with new and improved installations.

Reforming of straight-run naphthas is described by Leroi and Ferguson[10] as one of the important factors in raising the octane

[6] *Refiner*, 1933, **12**, 38.
[7] *Oil & Gas J.*, 1933, **32** (1), 8.
[8] *Oil & Gas J.*, 1934, **32** (35), 11.
[9] *Oil & Gas J.*, 1933, **31** (35), 20.
[10] *Oil & Gas J.*, 1933, **32** (1), 48.

rating of motor fuels. To this effect they review a series of experiment on reforming according to eight different types of operation, involving once-through operation, recycling, coil-only and "coil and soaker," at temperatures from 920° to 1025° F.

Some systematic studies of the composition of cracked gasoline have appeared. Martin, Gruse and Lowy[11] investigated the distribution of gum-forming constituents in cracked gasoline, and concluded that they are chiefly conjugated diolefins. Cyclic olefins are also thought to be gum-forming. Methods for determining the various types of hydrocarbons in cracked gasoline are offered by Nametkin and Robinzon[12] and by Tilitscheev and Masina.[13]

An interesting point in marketing which is related to the composition of cracked gasoline *vs.* the straight-run product is the fact that dyes which are satisfactory in the latter fade rapidly when used in cracked gasoline. This has been reported by Clarkson.[14]

In general, the continued progress of cracking during 1933 is noted in reports of meetings of scientific groups. Foster[15] finds that papers presented before the American Petroleum Institute reveal "new cracking procedures which surpass in flexibility and in quality of product anything yet discussed before a gathering of refiners." He also reports[16] a symposium on cracking at the American Chemical Society meeting.

Another striking proof of the definite place cracking has made for itself is the appearance of simplified expositions on the subject for the interested non-technical man. One such description is presented by Byler[17] and another by Marcotte.[18]

A review of the position of cracking in the broad picture of the oil industry is presented by Kessler,[19] who cites a "legitimate" and an "illegitimate" demand for liquid fuels—the latter to be fulfilled only at ruinously low prices. "Before the days of cracking," he says, "an illegitimate demand for fuel oil was of little moment, but just as soon as this cheap liquid fuel became a raw material for the production of gasoline, the danger arose, and with the modern development of the cracking process this danger

[11] *Ind. Eng. Chem.*, 1933, **25**, 381.
[12] *Neft. Khoz.*, 1933, **24**, 292; *Chem. Abs.*, 1933, **27**, 5953.
[13] *Khim. Sost. Neft. Neftyan. Prod.*, 1932, **23**, 161 *B.C.A.*—*B*, **1933**, 659.
[14] *Oil & Gas J.*, 1933, **31** (45), 50.
[15] *Nat. Petr. News*, 1933, **25** (21), 21.
[16] *Nat. Petr. News*, 1933, **25** (37), 68.
[17] *Diesel Power*, 1933, 11, 86.
[18] *Arts et Métiers*, **1933**, 166.
[19] *World Petr. Congr.*, 1933, II., 929.

is very real." He points out that production of unprofitable fuel oil must be reduced and cites the following theoretical possibilities:

"1. The maximum possible reduction of 86 per cent. is obtainable by cracking all straight-run fuel oil to coke.
"2. By a combination of hydrogenation and cracking, a reduction of 70·5 per cent. can be secured.
"3. By cracking all straight-run fuel by current composite methods a reduction of 47 per cent. is possible.
"4. By cracking all straight-run fuel by the low level system a reduction of 30 per cent. is obtainable."

The relative merits of these remedies are discussed and it is recommended to "crack to the maximum extent wherever there is a profit, reducing, if necessary, the production of crude oil accordingly."

Another suggestion for improved economy by cracking is made by Muishkin,[20] who recommends coverting larger amounts of oil into gasoline and other products.

II. Cracking Outside the United States.

The increase of refining, and especially of cracking operations, in countries outside the United States has been striking during 1933, and promises to continue at an increased rate. Legislation fostering home industries and discouraging importation of finished products is largely responsible for this growth of the cracking art in foreign countries.

The increased consumption of gasoline in France is noted by Kapcevitch,[21] who lists a few of the outstanding factors favouring the extension of cracking in France: (1) Continuous increase of consumption of gasoline and demand for higher anti-knock motor fuel; (2) absence of a market for heavy residues; (3) desire to minimise crude imports. The cracking capacity of French refineries in 1933 is reported to be from 40 to 50 thousand brls. per day, while a live problem at present is the utilisation of the by-products of cracking. Mockler[22] describes one of the new refineries in France which includes a cracking still, a viscosity breaker and a naphtha reformer. The cracking plant handles gas oil, crude oil and distillate from the crude distillation units. The capacity of the complete refinery is 5000 brls. per day.

The refineries of Compagnie Française de Raffinage are described[23] as comprising 6000 brls. per day of cracking capacity.

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[20] *Neft. Khoz.*, 1933, **24**, 250; *Chem. Abs.*, 1933, **27**, 5953.
[21] *Oil & Gas J.*, 1933, **31** (34), 16.
[22] *Oil & Gas J.*, 1933, **31** (36), 8.
[23] *Oil & Gas J.*, 1933, **32** (4), 12.

Belgium has followed the example of France in encouraging home refining by legislation. As a result, the cracking art also flourishes there, and a review of the refining industry of Belgium[24] shows a cracking capacity of 1400 brls. per day divided among three companies. One refiner runs coal tar as well as crude oil and petroleum residue, employing a unit of 300 brls. per day capacity and operating under 30 atmospheres pressure. A vapour-phase cracking unit of 100 brls. per day is used by a second company which cracks either gas oil or fuel oil by the aid of catalysts. Residue from this process is a commercial grade of asphalt, while the cracked gases are converted into alcohols—30,000 litres iso-propyl alcohol per month, 5000 litres butyl, and 1000 litres amyl. The third company operates a 1000 brls. per day cracking installation.

Economics and national policies also favour the growth of refining, and therefore of cracking, in Germany. Leonhardt[25] discusses the growth of refining in Germany. Similarly, the Italian cracking industry is reviewed by Mazetti,[26] while the economics of cracking in Rumania are discussed by Henri.[27]

Kimura[28] emphasises the importance of gasoline as a motor fuel in Japan. One-tenth of the Japanese gasoline is of domestic production, but this figure is to be increased. Maximum yield of gasoline from the crude oil is obtained by operation of modern cracking units.

III. The Cracking Reaction.

Increasing interest has been shown for several years in the fundamental scientific factors governing the cracking reaction, and in the effect of single variables and groups of variable conditions upon the direction of reaction. Continued interest in this subject and an increasing variety of studies of these factors is apparent in the publications for the past year.

Gary, Rubin and Ward[29] have determined the total heats of four gas oils at elevated temperatures (500–1000° F.) in both liquid and vapour states. They conclude that: (1) Weir and Eaton's equation, checked by this present work, is satisfactory for total heat of vapours at low pressures for all types of stocks, both virgin and cracked: $H=(215-87d)+(0{\cdot}415-0{\cdot}104\ d)t+(0{\cdot}000310-0{\cdot}000078d)t^2$ where H=total heat above 32° F., B.Th.U./lb.; d=specific gravity at 60° F., t=temperature °F.;

[24] *Oil & Gas J.*, 1933, **31** (45), 73.
[25] *Petr. Times*, 1933, **30**, 639.
[26] "Progressi Ind. Chim. Ital. I. Decennis Regima Fascista," 1932, p. 171; *Chem. Zentr.*, 1933, **104**, 1712.
[27] *Rev. Petrolifère*, 1933 (511), 8.
[28] *J. Fuel Soc. Japan*, 1933, **12**, 41; *Chem. Abs.*, 1933, **27**, 3808.
[29] *Ind. Eng. Chem.*, 1933, **25**, 178.

(2) the Bureau of Standards equation for specific heats of liquid petroleum is most reliable for virgin stocks; (3) the equation derived from the present data for liquids is satisfactory for gas oil and refractory cracking stocks from 40° to 15° API: $H=(15\,d-27)+(0{\cdot}7615-0{\cdot}400d)t+(0{\cdot}000625-0{\cdot}000440d)t^2$.

A heat flow diagram of a cracking still has been prepared by Vandenberg[30] based on elaborate heat balance calculations. The diagram is interpreted as showing that large quantities of heat are involved, compared with the small amount that finally goes into actual distillate vapours. It is also suggested that probably a larger amount of heat is dissipated by radiation than is usually suspected, and that this is due to high temperatures and large quantities of heat stored in circulating stock. Hot tar is thought to carry off most of the supplied heat, and this point seems to call for efficient heat exchange.

The influence of cracking conditions on the composition and reaction properties of cracked gasoline is discussed by Sager.[31] He finds that rapid and complete removal of the liquid phase from the reaction chamber and increased heat consumption per ton of crude oil changed the yield of gasoline from 42 per cent. of a product containing 7·2 per cent. olefins, 36·1 per cent. aromatics, 16·0 per cent. naphthenes and 40·7 per cent. paraffins to 35 per cent. of a product containing 18·2 per cent. olefins, 48·8 per cent. aromatics, 13·5 per cent. naphthenes and only 19·5 per cent. paraffins.

Berl and Dienst[31a] also investigated the effect of temperature, time and pressure in cracking. They reported experiments on gas oil (boiling range 245—355° C.) under conditions of 400 and 425° C., and 18 and 24 atmospheres, with reaction times of 60, 180 and 300 min. to be "corrected for 10 min. time required to pump the cracking oil through the heating tube to the pressure vessel." Experiments were carried out in "liquid-phase," using a pressure bomb of 900 c.c. capacity. Experimental results were as follows:—

Experiment number	1	2	3	4	5	6
Temperature ° C.	425	425	425	400	400	400
Pressure (atm.)	24	24	24	18	18	18
Corrected reaction time (min.)	70	190	310	70	190	310
Total yield cracked products (per cent.)	10·2	25·4	32·6	2·2	5·9	8·3
Composition cracked gasoline:—						
Unsaturates (per cent.) ..	20	19	16	15	18	20
Aromatics (per cent.) ..	16	13	16	20	18	17
Naphthenes (per cent.) ..	0	8	6	5	3	5
Paraffins (per cent.) ..	64	60	62	60	61	58

[30] *Oil & Gas J.*, 1933, **32** (12), 13.
[31] *Petr. Times*, 1933, **29**, 549, 619; *Petr. Z.*, 1933, **29** (15), 1.
[31a] *Petr. Z.*, 1933, **29** (32), 1.

Philippide[32] cracked kerosine in an electrically heated tube at 600° C. at different pressures and with different rates of throughput, both with and without catalysts of Al_2O_3 and fuller's earth. Increased pressure caused increased yields of oil boiling up to 200° C. with a drop in specific gravity and percentage of unsaturated constituents. The yield was also increased by the presence of the catalysts.

Variation of pressure was also studied by Kato,[33] who noted that loss due to carbon deposition and uncondensable gas increases with pressure especially over 200 atmospheres. He also indicated that both cracking rate and gasoline yield decrease with pressure increase, while the degree of unsaturation of the gasoline also decreases.

By a detailed study of once-through cracking of Mid-Continent virgin gas oil, the effect of time, temperature and pressure on the rate of formation of gasoline and gas was indicated in data presented by Keith, Ward and Rubin.[34] They report 71 runs under pressures of 100 to 1000 lb./sq. in. at temperatures from 800 to 1100° F., and from 3 to 42 per cent. cracking per pass. Time above 800° F. varied from 10 to 440 secs. Besides tabular and graphed data, the experimenters summarise their conclusions as follows :—

"1. If cracking conditions are so maintained that tar formation is minimised, the general equation for a mono-molecular reaction can be utilised satisfactorily to correlate the data when the amount of material cracked is expressed in terms of gasoline plus gas as a function of time.
2. Within the limits studied, pressure has no effect on the reaction rate as defined.
3. The amount of fixed gas per unit of gasoline produced varies inversely as the pressure.
4. The amount of gas produced is not necessarily a measure of the octane number as measured by the C.F.R. Motor Method, and for a given octane number as measured by this method, the higher the pressure, the smaller the gas-gasoline ratio."

Groll[35] emphasised that quality and yield of products of vapour-phase cracking are functions of temperature and rate of throughput, and these two variables were found to be connected by a simple function over a comparatively wide range.

Mariotti[36] also studied the influence of temperature and rate of

[32] *Petr. Z.*, 1932, **28** (51), 1.
[33] *J. Soc. Chem. Ind. Japan*, 1933, **36**, 226B ; *Chem. Abs.*, 1933, **27**, 3808.
[34] *Proc. A.P.I. Sec. III.*, 1933, **14**M, 49.
[35] *Ind. Eng. Chem.*, 1933, **25**, 784.
[36] *L'ind. Chimica*, 1933, **8**, 4 ; *B.C.A.—B*, 1933, 338.

flow in cracking on the yield and quality of the gas obtained. His charge was Ragusa oil. Best results were obtained by treatment of the fraction boiling at 186—360° C., at temperatures no higher than 800° C. Higher temperatures caused decomposition of the lighter products to carbon and hydrogen.

The effect of type of flow in the process of producing olefins from the paraffins (ethane to heptane) is reported by Cambron and Bayley.[37] They indicate that turbulent flow greatly increased the yields of olefins compared with operation in streamline flow. Higher rates of conversion are also noted, and the pressure drop in the tube varies with the square of the gas velocity rather than directly with the velocity.

Nelson and Egloff[38] have noted the effect of cracking stock on the gasoline obtained. They recommend direct cracking of crude oil instead of topping and cracking.

A comparison of pressure-cracking and hydrogenation processes applied to Alberta bitumen for production of motor fuel is made by Warren.[39] Yields of gasoline were "slightly" higher with cracking than with batch hydrogenation. The yield of coke from the cracking process, however, is presented as an offsetting disadvantage. Warren claims technical advantages for hydrogenation, but cites the fact that the economic balance is in favour of cracking from the viewpoint of various costs.

A similar comparison of cracking and hydrogenation products is offered by Haslam, Russell and Asbury,[40] who report yields and octane numbers of gasolines from five charging stocks processed by both methods. The essential differences indicated are that cracking produced 15–49·5 per cent. of 12° API residuum, whereas no residuum was obtained by hydrogenation; cracking yielded 66–85 per cent. as much gasoline as high temperature hydrogenation and 50–75 per cent. as much as low temperature hydrogenation, while octane numbers were 10 per cent. and 20 per cent. higher respectively for cracking.

IV. Liquid-Vapour Phase Cracking.

A. Non-Catalytic.

The variety of stocks by the cracking process into high yields of anti-knock gasoline and valuable residues continues to be stressed during the current year of 1933.

A new Dubbs cracking unit in Texas is described by Ziegenhain.[41] This unit uses dual furnaces and has been proved to be able to

[37] *Can. J. Research*, 1933, **9**, 175.
[38] *Petr. Z.*, 1932, **28** (51), 6.
[39] Canadian Dept. of Mines, Mines Branch, **Paper 725, 1932.**
[40] *Refiner*, 1933, **12**, 370.
[41] *Oil & Gas J.*, 1933, **31** (35), 22.

handle cracking stocks, including 24·5 API gravity Refugio crude oil, 24 gravity E. Texas bottoms, p.d. bottoms, gas oil, 48 gravity naphtha, and naphtha of 52° API gravity. Yields from cracking pressure distillate bottoms are 50 per cent. of cracked gasoline of 72 octane number and from cracking naphtha, 80–85 per cent. of 78–80 octane number. A reforming unit operated by the Dubbs process[42] has also been put into operation, converting 9000 brls. per day of straight-run gasoline and 5200 brls. per day of "straight-run naphtha." "Very satisfactory results" are reported. A recent Dubbs unit, operating in Germany, has been described by Wagner.[43] A yield of 40 per cent. of cracked gasoline from topped crude is accompanied by a good asphalt and valuable cracked gases.

The nature of the products obtained by the application of the Dubbs cracking process to different kinds of charging stocks has been widely illustrated by additions to the series of articles continued over several years by Egloff and Nelson.[44] Under cracking conditions of moderate temperature and pressure, varying according to the charge but applied in the same unit, high yields of good anti-knock gasoline were obtained from varied oils accompanied by cracked residues suitable for excellent fuel oil. The additions this year comprise oils from Trinidad, Mexico and California, including crude oil, topped crude, reduced crude, gas oil, kerosine, naphtha and pressed oil, as well as shale oil from Esthonia and seal oil from Alaska. The yields and octane number of the cracked gasolines are listed in the table :—

Charging stock.	Source.	Gasoline % of charge.	Octane number.
Crude Oil	Trinidad	55·1 ..	85
" "	Mexico (Naranjos) ..	40 ..	67
Topped crude ..	Trinidad	45·6 ..	87
" " ..	California :— Elwood, Signal Hill, Santa Fé } blend ..	58 ..	73
Press Oil	Mexico (Naranjos) ..	58 ..	77
Reduced crude ..	California :— Elwood, Signal Hill, Santa Fé } blend ..	38·9 ..	72
Gas oil	Trinidad	58·9 ..	91
Kerosine	Mexico (Naranjos) ..	73·8 ..	71
Naphtha	" " ..	83 ..	69
Crude shale oil ..	Esthonia	42·7 ..	73
Topped shale oil ..	"	27·4 ..	74
Seal oil	Alaska	59·9 ..	66

[42] *Petr. Times*, 1933, **30**, 658.
[43] *Automobiltech. Z.*, 1933, **36**, 160.
[44] *Oil & Gas J.*, 1933, **31** (34), 14; (37), 12; (42), 16; *Petr. World*, p. 19 (March, 1933); *Petr. Z.*, 1933, **29** (17), 5; *Petr. Times*, 1933, **29**, 359; *Ind. Eng. Chem.*, 1933, **25**, 386.

Egloff and Nelson[45] have also prepared a résumé of the results of cracking many kinds of stocks, including straight-run gasoline, naphtha, gas oil and fuel oil. They note that no advantage is gained, as far as yield and octane number of gasoline is concerned, whether the straight-run gasolines or naphthas are cracked separately or not. Using gas oil charges from Pennsylvania, Mid-Continent, East Texas, Coastal and California, the octane number of the cracked gasoline was noted to depend upon the source of the stock when cracking conditions were similar. Yields of gasoline from Smackover topped crude were especially cited as examples of the effect of operating conditions since the anti-knock value of 80 octane number was maintained with gasoline yields ranging from 39 to 63 per cent. Flexibility in the cracking process is emphasised in the description of light and heavy oil cracking, in which the naphtha fraction is converted in one heating coil and the fuel oil residue in another, after first topping out a light gasoline fraction of high anti-knock value. East Central Texas crude oil yielded 68·5 per cent. of 75 octane gasoline.

The cracking of East Texas residuum under 350 lb. pressure at 900° F. has been found by Trusty[46] to give a "high yield of distillate which may be treated with a small amount of acid and re-run to produce a low sulphur, low gum and good colour gasoline with a fairly high octane number." The actual octane number reported was 65, cracking operation being carried out in a tube and tank unit by the flash residuum method.

Piguzov[47] reported yields of about 30 per cent. gasoline, 22·3 per cent. kerosine, 15·3 per cent. gas oil, and 20·3 per cent. residue boiling above 300° C. (loss 12·7 per cent. including gas) from the cracking of Fergana gas oil at 450° C. under 40 atmospheres pressure. This was once-through operation. The gasoline yield increased to 42·6 per cent. after five recycle operations. Vacuum distillation of the cracked residues yielded 56·3 per cent. of a fraction boiling between 212 and 295° C., while the remaining bottoms included an asphalt of 40° softening point, penetration 47, and ductility greater than 120.

Gas oil distillate from Patagonia crude oil was cracked by the Cross process to yield coke, fuel oil, gasoline and gas. Dennis[48] has given a general description of the procedure.

Reforming, or cracking, a heavy naphtha into high anti-knock gasoline was described by Albright.[49] The stock had an initial

[45] *Refiner*, 1933, **12**, 217.
[46] *Petr. Eng.*, 1933, **4**, 34.
[47] *Acta. Univ. Asiae Mediae Tashkent Ser.* 1932, VI. (5), 8; *Chem. Abs.*, 1933, **27**, 4383.
[48] *Ind. Chem.*, 1932, **8**, 281.
[49] *Refiner*, 1933, **12**, 2.

boiling point of 300° F., and an end point of 475–500°, and was raised to a temperature of 1010°F. under pressure of 370 lb. The product had an octane number of 71, which decreased to 69 when the temperature of reforming was lowered to 998° F.

The coking method of cracking was applied to Grozny and Surakhani oils by Tilitscheev and Seledzhiev.[50] Under 5 atmospheres pressure, Grozny paraffin distillate produced 52 per cent. boiling under 200° C., 72 per cent. under 300° C., and 80 per cent. under 350° C. Surakhani fuel oil yielded 73 per cent. boiling under 300° while Grozny mixed-base fuel oil yielded 64 per cent., Grozny mixed-base bottoms 59 per cent., and cracked residue from Grozny mixed-base fuel oil 49 per cent.

A series of experiments by Tarasov and Seledzhiev[51] deals with the cracking of heavy ends left after distillation of pressure distillate. At 450° C. for 100–120 min. under 40 atmospheres pressure, a cracking stock (sp. gr. 0·824) yielded 9·3 per cent. gas, 23·3 per cent. boiling below 200° C., 59·6 per cent. 200–300° C. and 7·8 per cent. above 300° C. with once-through operation. One recycling changed these percentages respectively to 4·9, 13·4, 36·5 and 4·8 per cent., and this type of operation is recommended for commercial work.

Tarasov[52] reports a comparison of converting condensate from cracking and distillates from the cracked residue. The experiments were carried out in an autoclave at 30 atmospheres pressure and 450° C. for 40 minutes. "Carboid" formation was 0·028 per cent. when cracking distillate and 0·100 per cent. when cracking residue. The residue yielded slightly more gasoline, but kerosine and gasoline yields were 48·3 per cent. from the condensate, 56·3 from the distillate and 39·3 from the residue. At atmospheric pressure, cracking the residue yielded 35 per cent. gasoline.

A description of some cracking units in the United States has been published in Russia by Kevorokov.[53]

Cracking by means of a bath of molten metal, *e.g.*, lead, as patented by Bornemann and Weicksel, has also been described.[54] The process, carried out in a column of molten metal, comprises the mixing of oil and metal in both horizontal and vertical directions. Flexibility of yield is claimed by adjusting to "deeper" or "milder" cracking. Deep cracking yields "60 per cent. or more" of gasoline, much gas and an asphalt residue. Milder

[50] *Neft. Khoz.*, 1932, **23**, 47; *B.C.A.—B*, 1933, 135.
[51] *Neft. Khoz.*, 1932, **23**, 177; *Chem. Abs.*, 1933, **27**, 2022.
[52] *Neft. Khoz.*, 1933, **24**, 244; *Chem. Abs.*, 1933, **27**, 5953.
[53] *Onti-Aznefteizdat Baku*, 1932 (8), 115; *Chem. Abs.*, 1933, **27**, 833.
[54] *Petr. Z.*, 1833, **29** (4), 1.

cracking produces valuable high boiling products, *e.g.*, solvents and fuel oil, besides a "good" yield of gasoline.

B. Catalytic.

The use of catalysis in the liquid-vapour phase cracking of mineral oil has increased in the past year. Ivanyss[55] discusses the cracking of gas oil from Grozny crude in the "liquid-phase" under atmospheric pressure by the aid of catalysts. The catalysts used in his series of experiments included the metals zinc, tin, aluminium, iron, nickel and sodium, their oxides, hydroxides, carbonates and chlorides, Kieselguhr, activated charcoal and floridin. He concluded that, using 10 per cent. by weight of catalyst and heating at 324–327° C. for 3 hrs., practically the only active agents for gasoline production were aluminium chloride, aluminium (5 per cent.) and zinc. These produced yields of 42, 5·4 and 5·4 per cent. gasoline respectively.

According to Deisenhammer,[56] however, the use of 0·5 per cent. of activated carbon in the distillation of Zistersdorf petroleum increased the volume of distillate boiling up to 300° from 11·4 to 45 per cent. The corresponding increase in gasoline yield was from 1·4 to 8·1 per cent. with a "very small" gas loss.

Yields of 48 per cent. gasoline boiling at 50–200°, a 15 per cent. fraction boiling at 200–300°, and 18 per cent. above 300°, were reported by Zelinski and Mikhlin[57] from the cracking of Emba crude oil at atmospheric pressure with 10 per cent. aluminium chloride. Grozny paraffin, cracked at 130–140° in contact with finely ground aluminium chloride, yielded 55 per cent. gasoline, 25 per cent. asphalt and 20 per cent. gaseous products.

A process for cracking oil using a liquid metal such as mercury as a heating medium has been described by Oberle.[58] The metal is contained in a coil rather than in a bath, and he noted that the use of mercury entailed both a catalytic influence on the oil and a desulphurising effect.

V. Vapour-Phase Cracking.

A. Non-Catalytic.

Two installations of vapour-phase cracking units are reported to be in progress. One, at Tampico,[59] is designed to produce 1000 to 1500 brls. per day of finished gasoline. Another, in Louisiana, involves the construction of two units processing reduced crude.[60]

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[55] *Petr. Z.*, 1933, **29** (21), 1.
[56] *Petr. Z.*, 1933, **29** (17), 3.
[57] *J. Appl. Chem.* (*U.S.S.R.*), 1933, **6**, 16; *Chem. Abs.*, 1933, **27**, 5176.
[58] *Petr. Z.*, 1933, **29** (25), 1.
[59] *Oil & Gas J.*, 1933, **31** (52), 34.
[60] *Nat. Petr. News*, 1933, **25** (28), 10.

B. Catalytic.

The use of catalysis in connection with vapour-phase cracking of petroleum oils to obtain high anti-knock gasoline is the theme of a recent description of what is known as the "Houdry process."[61] The advantages of the process, which is in the experimental stage, are claimed to be: (1) Higher octane gasoline; (2) lower production cost; (3) a residual oil that is always a clean stock of gas-oil boiling range; (4) use of moderate temperatures and pressures only slightly above atmospheric. Octane numbers obtained vary from 75 (from Penna. fuel oil) to 85 (from Coastal distillate). Regeneration of the catalyst without removal from the system is claimed. Another description of the same process[62] indicates that, operated in combination with "thermal" cracking, "73 per cent. of an 11 lb. Reid gasoline of an octane number of nearly 73 has been made with less than 9 per cent. of Bunker C fuel oil as final residuum."

VI. Combination Liquid-Vapour and Vapour-Phase Cracking.

A 32,000 brl. cracking unit combining the use of liquid-vapour and vapour-phase cracking is described by Armistead[63] for processing crude oil completely. Primary cracking is carried out on reduced crude in the liquid-vapour phase. The vapour-phase cracking is carried out on stock from the base of the bubble tower, boiling range being carefully regulated for suitability to vapour-phase temperatures. Heavy straight-run naphtha from the crude is reformed in the same plant at 1000° F. under 500 lb. pressure. Total gasoline obtained from a 36–37° API Mid-Continent crude was 66·2 per cent., including 15·7 per cent. light straight-run gasoline. The remaining product was 24·8 per cent. fuel oil and 9 per cent. represented gas and loss.

VII. Cracking with Oxidation.

A general discussion of the role of oxygen in the cracking of hydrocarbon oils is offered by Beall.[64] He supports an "oil-gas conversion process," employing oxidation and claims that it lowers cost of raw material by using natural gas or cheap hydrocarbon gas, increases yield by using high pressures and improves quality by operating in vapour-phase. It is explained that the admixture of oxygen to the gas being cracked lowers the temperature of chemical change. The oxygen combines with some hydrogen, with some carbon, and with carbon compounds which are then

[61] *Oil & Gas J.*, 1933, **32** (22), 12.
[62] *Nat. Petr. News*, 1933, **25** (52), 27.
[63] *Oil & Gas J.*, 1933, **32** (24), 11.
[64] *Refiner*, 1932, **11**, 606.

cracked. The exothermic nature of oxidation raises the reaction temperature high enough also to crack the original hydrocarbon gas. Thus, with sufficient oxidation, Beall claims that the possibilities of synthesis, re-arrangement and decomposition are extended over those obtained without addition of oxygen.

Matignon and Léon[65] report the catalytic conversion of gasoline and heavy fuel oil into gaseous mixtures by excess of steam. The temperature was 1000° C., time 0·3 to 2·0 secs., and catalyst ZrO_2. The gaseous products contained 76·2 and 67·9 per cent., respectively, of hydrogen.

VIII. Electrical Cracking.

The electric arc was used by Fester, Filippo and Patrone[66] as a cracking medium to produce olefins for synthesis. Iron arcs in kerosine gave 35·7, 34·0 and 27·5 per cent. ethylene, and 1·0, 0·7 and 4·2 per cent. acetylene; in gas oil 12·8 per cent. ethylene and 0·6 per cent. acetylene. Copper arcs in kerosine gave 46·7 per cent. ethylene and 7·9 per cent. acetylene.

IX. By-Products of Cracking.

In spite of the original domination of gasoline as the primary important product from cracking, the number and importance of the so-called by-products of the process have grown to undeniably great proportions. In many cases these products have ceased to be by-products at all, but have become the end toward which the conditions of cracking are regulated.

Alcohols of many kinds are available from cracked petroleum hydrocarbons. Brooks[67] has presented a survey of the literature on converting olefins from the cracking process into ethyl, isopropyl, butyl, amyl and hexyl alcohols. These alcohols are being produced on a commercial scale from cracked gas. A specific example of the development of alcohol synthesis from cracked products, as reported by a "large chemical company,"[68] was based on the desire to utilise fully the large quantities of ethylene made at relatively low cost in the hydrocarbon cracking processes being operated by that company.

An example of a cracking process which is operated specifically to produce another primary product than gasoline has been described by Gerr, Pipik and Mezheborskaya.[69] They note that this process yields 20 per cent. ethylene in the cracked gas as

[65] *Compt. rend.*, 1933, **196**, 513.
[66] *Rev. facultad quim. ind. agr. Univ. nacl. litoral*, 1932, **2**, 130; *Chem. Abs.*, 1933, **27**, 5954.
[67] *World Petr. Congr.*, 1933, **2**, 840.
[68] *Chem. Met. Eng.*, 1933, **40**, 567.
[69] *Refiner*, 1933, **12**, 70.

compared with 12–14 per cent. from ordinary "liquid-phase" processes and 14–18 per cent. from vapour-phase processes. The ethylene is produced in order to be converted into ethyl alcohol.

The same process was applied on a semi-commercial scale by Dalin and Gutuirya[70] to manufacture ethyl alcohol from ethylene obtained from cracked gases. The alcohol obtained was 90 per cent. and the yield varied from 5·5 to 6·2 per cent.

The preparation of butyl alcohol from cracked gases has also been investigated.[71] The method used by the experimenters was treatment with sulphuric acid in the cold (–10° C.). With acid of 50–55 per cent. strength, it was found that the best alcohol yield of 4–9 per cent. was obtained without simultaneous formation of polymers. Less polymers and more alcohols but of the higher boiling range were obtained using 75 per cent. acid. The optimum treating time was 12 hrs., a shorter period yielding less alcohol and less polymers. Lowered temperatures decreased polymer formation, but it could not be eliminated.

The production of alcohols as well as other oxygenated products from cracked hydrocarbons has been described by Newitt and Townend.[72] Their "typical" cracked gas contained 2·9 per cent. H_2, 64·5 per cent. CH_4, 16·0 per cent. C_2H_6, 6·7 per cent. C_3H_8, 2·9 per cent. C_4H_{10}, 2·9 per cent. C_2H_4, 1·9 per cent. C_3H_6, and 1·3 per cent. C_4H_8. They found that methane, at 106·4 atmospheres and at 341° C. yields 22·3 per cent. of "nearly pure" methyl alcohol. From ethane, at 100 atmospheres and 272° C., 71·7 per cent. of the hydrocarbon burnt yielded condensed products as follows: 51·0 per cent. ethyl alcohol, 28·0 per cent. methyl alcohol, 11·1 per cent. acetaldehyde, 9·0 per cent. acetic acid, 0·3 per cent. formaldehyde, and 0·6 per cent. formic acid.

Gas from the cracking process has continued to extend and multiply its uses. McBride[73] reviews its application as a part of the refinery gas used to enrich a city gas supply. It may be used for cold carburetting water gas, to yield lightly carburetted water gas, or to be cracked—*i.e.*, reformed. In the last case, lighter hydrocarbons are produced as a substitute for enriching oil, and free carbon is deposited to become a solid fuel to substitute for the coke ordinarily used.

For domestic heating, as suggested by Vuiborova and Kalininskaya,[74] cracked gas must be desulphurised and all non-gaseous hydrocarbons removed. Its high heating value is then available for home heating.

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[70] *Azer Neft. Khoz.*, 1933 (3), 66; *Chem. Abs.*, 1933, **27**, 4211.
[71] *Refiner*, 1933, **12**, 27.
[72] *World Petr. Congr.*, 1933, **2**, 847.
[73] *Chem. Met. Eng.*, 1933, **40**, 508.
[74] *Groznenskii Neftyanik*, 1932, **2** (9–10), 59; *Chem. Abs.*, 1933, **27**, 4057.

The polymerisation of olefins, of which a high percentage is contained in cracked gases, to produce liquid fuels has been applied in several directions. Gasoline may be the product, lubricating oils may be formed, or special fuels such as Diesel oil may be obtained.

Bowen and Nash[75] review the formation of liquid motor fuels by polymerisation of olefins from cracked gases. The polymerisation of gaseous olefins at moderate temperatures under pressure, without catalysts, yields a "crude oil" containing a high proportion of gasoline. The oil is not aromatic and contains paraffins, naphthenes and higher olefins—*e.g.*, hexenes—in considerable quantity. At high temperatures, without catalysts, largely aromatic oils are obtained from the gaseous olefins, yielding high anti-knock gasoline.

Bowen and Nash also discuss the polymerisation of olefins, especially ethylene, under pressure with aluminium chloride to form lubricating oils and high anti-knock gasoline. At 10–15° C., the oil obtained is heavier than that formed at 150° C. The gasoline obtained is practically wholly paraffinic and has an octane number between 70 and 80. The hydrocarbon constituents are thought to be largely branched-chain.

The polymerisation of "ethylene concentrate" from cracked gases in the presence of aluminium chloride is also the subject of experimentation by Petrov, Antzuz and Pozhiltzeva,[76] although they are primarily interested in the production of lubricating oils. The original concentrate contained 20–33 per cent. olefins and the balance was hydrogen and methane. Condensates were prepared at room temperature and at 100° C. Those formed at room temperature were composed of a smaller number of compounds than natural oils. In viscosity, they compare with synthetic oils prepared with boron trifluoride. The condensation at 100° C. went much faster than at room temperature. Unsaturated aromatic hydrocarbons formed 20 to 40 per cent. of the product.

Diesel oils produced by polymerisation of olefins from cracked gases in the presence of catalysts are suggested by Howes,[77] although he notes that no actual engine tests have been made on such oils for Diesel fuels.

Another important application for ethylene obtained from cracked gases is in the plastic resin industry to displace cellulose products, pyroxylin and phenolic resins as reported by Migey.[78] The "metastyrene resin," produced from ethylene, is described as

[75] *World Petr. Congr.*, 1933, **2**, 774.
[76] *J. Appl. Chem. U.S.S.R.*, 1932, **5**, 790; *Refiner*, 1933, **12**, 292.
[77] *World Petr. Congr.*, 1933, **2**, 781.
[78] *Refiner* 1932, **11**, 547.

having decided advantages over the older products of the resin industry. It is noted that the resin can be produced for less than 12 cents a lb., the cost of pure ethylene from cracked gases being calculated at 4·6 cents per lb.

Asphalt from petroleum cracking processes is coming increasingly into demand. A cracking installation specifically adapted and regulated to the processing of residues to produce asphalt has been described recently.[79] The suitability to various uses of asphalts from cracking is discussed by Abson,[80] who indicates that, at present, they are suited to most asphalt purposes with the exception of hot-mix paving. They may be applied alone or in blends. It is prophesied that improvements in cracking will be directed to controlling the quality of residuum, and cracked asphalt will be equal or even superior to the straight-run product. At present, cracked asphalts make better "cut-backs" and emulsions than straight-run asphalt. Many refineries are marketing cracked asphalt as such or blended with straight-run asphalt.

Taylor[81] reports experiments to show that the quality of asphalt from cracked residues can be varied under control between the limits of 0–30 penetration by increasing the quantity of gas oil converted into asphalt, and that residual oils from non-asphaltic base can be made to give asphalts with a wide range of properties, yields varying from 50 to 95 per cent. by weight. It was found that air-blowing in place of steam refining increased yield and improved the quality of the product, although reaction time was lengthened. Agitation also raised the yield and improved the penetration value of the product.

The increasing percentage of cracked products in the Bunker C fuel oil being marketed is discussed by Stillman.[82] Cracked fuel oil has been found to retain the proper viscosity for atomisation at 175° F. oil temperature. Moreover, cracked fuel is excellent for power purposes, being high in B.Th.U. value. Having lower viscosity than uncracked oils, they require less live steam per gall. for preheating. Stillman suggests the treatment of cracked residues at the refinery to remove impurities and so improve stability. The discussion of Stillman's paper includes some comments by Goodwin, who cites recent experiments on chemical treatment of cracked residues to remove unstable solids. He points out that the advantages of cracked fuel include a saving in preheat due to viscosity break at 130–155° F., a pour point of 0° F., and lower gravity giving more pounds per gallon.

[79] *Refiner*, 1933, **12**, 83.
[80] *Oil & Gas J.*, 1933, **31** (45), 69.
[81] *Ind. Eng. Chem.*, 1932, **8**, 429.
[82] *Power Plant Eng.*, 1932, **36**, 711.

On the contrary, Russell and Hanks[83] emphasise the excess supply of fuel oil available and recommend modification of refinery operation in order to yield less fuel oil per volume of gasoline, partly by cracking to heavier residues.

Coke is another valuable fuel obtained from the cracking process by what is known as a non-residuum method of operation. A handling and conveyor system, operated by one man, to handle 65 tons per day of Dubbs' coke has been described.[84]

A relatively new field for the invasion of cracked products is the special solvents industry. Conine[85] points out that favourable results have been obtained with closely fractionated distillates from vapour-phase cracking units and gas polymerisation units to be used as special solvents, although no test data have been published as yet. The new cracked special naphthas are expected to be rich in aromatics and unsaturates but not gum-forming. A tendency to employ these solvents in the manufacture of varnish, paints and lacquers directly at the refinery is noted.

The general chemical industry, too, may be supplied with valuable products obtained from cracked oils. Sucharda and Mazonski[86] report the preparation of amyl and hexyl formates from cracked gasolines containing 22·4 per cent. unsaturates. The cracked gasoline was reacted slowly with anhydrous formic acid in the presence of a small amount of sulphuric acid. Cyclic operation yielded almost complete conversion of formic acid into the formates of secondary and tertiary amyl and hexyl alcohols. The presence of sulphuric acid suppresses polymerisation of the olefins.

X. Modernised Cracking-Plant Arrangement.

New cracking plants continue to increase in number, and more and more attention is being given to co-ordinating their operation with the balance of the refinery. Willson[87] describes a new plant which combines topping and cracking in one continuous operation with a commercial grade of fuel oil as the only residual product. The refinery has a capacity of 3500 brls. per day, and the cracking operation is carried on at 400 lb. pressure and 1000° F.

A new set of cracking units discussed by Chatfield[88] is claimed to show great flexibility in conjunction with a common reflux system. The units are designed to operate either for high octane rating or maximum yield as market conditions may demand. A viscosity breaker and vapour-phase furnace comprise the double

[83] *Oil & Gas J.*, 1932, **31** (28), 14.
[84] *Refiner*, 1932, **11**, 531.
[85] *Oil & Gas J.*, 1933, **31** (45), 66.
[86] *Przemysl Chem.*, 1933, **17**, 41 ; *Chem. Abs.*, 1933, **27**, 5954.
[87] *Oil & Gas J.*, 1933, **31** (42), 10.
[88] *Nat. Petr. News*, 1933, **25** (42), 32.

furnace, charge to the latter being controlled at 25·8° API, initial boiling point 218° F., and maximum boiling point 632° F. Long runs under severe cracking conditions are claimed.

A third new modern plant, described by Foster,[89] includes "three major principles of refining economy:" topping crude by waste heat; cracking different fractions in different coils under optimum conditions for each; and vapour-phase chemical treatment. Ziegenhain[90] describes this same refinery in which waste heat from cracking is used for topping the crude. The plant "emphasises the trend toward making the cracking unit the principal equipment in the refinery around which all other processing equipment is built." Both cracking and reforming are employed, the former at 925° F. under 400 lb. pressure and the latter at 985° F. under 300 lb. The average octane number of the cracked gasoline obtained is 70.

Willson[91] comments upon the expansion of modern refining in Kansas with the recent completion of two new plants employing the latest cracking installations.

In addition to the construction of new refineries, a number of existing cracking plants have been improved and modernised with new equipment. A reforming unit at a Pennsylvania refinery, described by Robinson,[92] has been reported to be remarkably successful. A yield of 80 per cent. of 74 octane gasoline is claimed from straight-run gasoline charge. It was found that, using the reforming unit in conjunction with the other cracking facilities of the refinery, a yield of 49·5 per cent. of 70 octane gasoline was obtainable from the crude oil.

Revamping a Canadian cracking plant is reported by Foster[93] to add 66 per cent. to the gasoline yield. "The plant was revamped as a combined skimming and cracking plant incorporating the Dubbs principle." Replacements and additions affected the furnace design, tubes, headers, reaction chamber, flash chamber, bubble tower and heat exchangers. Similarly, in another refinery described by Johnson,[94] addition of equipment to a cracking plant in order to permit segregated coil cracking resulted in a product of much improved quality. Still another case of revamping[95] replaces an old cracking unit with a modern installation to yield high anti-knock gasoline.

A combination installation for topping, cracking, stabilising,

[89] *Nat. Petr. News*, 1933, **25** (23), 26.
[90] *Oil & Gas J.*, 1933, **32** (6), 14.
[91] *Oil & Gas J.*, 1933, **31** (39), 15.
[92] *Oil & Gas J.*, 1933, **31** (45), 56.
[93] *Nat. Petr. News*, 1933, **25** (29), 32.
[94] *Refiner*, 1933, **12**, 203.
[95] *Nat. Petr. News*, 1933, **25** (8), 14.

redistilling and treating is the subject of an article by Jirasek and Schaeffer.[96] The unit operates on Mid-Continent crude, and is described in some detail as added information for the German refiner. For a similar purpose Walther[97] reviews a number of means for disposing of the coke formed in some of the older pressure cracking operations.

Important in the efficient operation of a cracking plant is the accompanying experimental work to develop new and improved methods of processing and to indicate new design for equipment. A laboratory pilot cracking unit serving this purpose is reported by Gary and Ward,[98] who claim that in it "practically all commercial types of cracking processes may be duplicated."

Other aids to efficient refinery operation are modern sources of power, as described by Ziegenhain,[99] and the use of adequate automatic control and regulatory instruments such as those suggested by Chadbourne.[100]

XI. Cracking Equipment.

With the development of the method of operation of cracking processes, the problem of apparatus of proper design and materials of sufficient strength has become more acute. The matter of design of apparatus has received more study, and new types of equipment have been developed in the past year to keep pace with the advance of the cracking process.

A series of typical design calculations for cracking equipment is offered by Nelson[101] based on recycle ratios, pressure, temperature, time, heat balances, and other pertinent factors. Another general method for designing apparatus to handle hydrocarbon mixtures at high temperatures has been suggested by Lewis and Luke.[102] Truesdell[103] has particularly noted the development of new principles of refinery equipment design as brought out in a symposium at the American Chemical Society meeting. New bases for design of stills, fractionating towers, furnaces and heat exchangers were cited.

A specific design for a modern recirculation pipe still is presented by Nelson,[104] who claims greater efficiency for it than for a simple radiant type still.

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[96] *Petr. Z.*, 1933, **29** (46), 1.
[97] *Erdöl u. Teer*, 1932, **8**, 543.
[98] *Oil & Gas J.*, 1933, **32** (1), 53.
[99] *Oil & Gas J.*, 1933, **31** (45), 49.
[100] *Refiner*, 1933, **12**, 200.
[101] *Petr. Eng.*, 1933, **5** (2), 78.
[102] *Petr. Mech. Eng.*, Sept. 15, 1932, 55.
[103] *Nat. Petr. News*, 1933, **25** (14), 12.
[104] *Petr. Eng.*, 1933, **4** (10), 23.

Singer[105] describes the world's largest reaction chamber built in England for high temperature, high pressure use. Laboratory apparatus for experimental cracking has also been improved, as exemplified in a laboratory cracking furnace described by Dick,[106] and a cracking train for studying hydrocarbon decomposition products, described by Jelinek.[107]

Materials suitable for withstanding the strain of severe modern cracking conditions are of equal importance with design in new cracking equipment. Malcolm[108] lists the following primary characteristics on which selection of such materials must be based: chemical resistivity, creep resistance, thermal expansion, resistance to scaling and oxidation and resistance to wear. "Ratings" for materials of various kinds are discussed. Requirements in materials for high temperature, high pressure equipment are also reported by Kanter & Maack.[109] They conclude that steel is necessary for most valves and fittings under high pressure at high temperature, although especially severe conditions call for alloying or special heat treatment.

A number of the problems of the pressure vessel user were discussed thoroughly by Jasper, Andrus and Larsen[110] at a metallurgical symposium. They included such matters as the various methods of fabrication. Autogenous welded vessels mark the most recent development. The effect of pressure vessel design on economy and safety in processing is emphasised, since this is the most hazardous part of cracking units.

Duff[111] presents a discussion of the metallurgy of refining equipment applied to the suitability of alloys and metals for cracking still tubes, heat exchanger tubes, condenser pipe, return headers, flanges, bolts, tube hangers, pressure vessels, fittings, etc. In the same symposium, Foley[112] discusses the characteristics of steel under the conditions of heat and corrosion such as those met in a refinery. He classifies alloy steels for cracking and similar equipment into corrosion-resisting and heat-resisting types. Plain carbon steels are suitable at 850° F., low alloy pearlitic steel at 1100° F., and high alloys above that.

Safety in a cracking plant is a matter of outstanding importance that has been carefully studied. Murphy[113] notes that an indi-

[105] *Petr. Z.*, 1933, **29** (4), 10.
[106] *Am. Gas J.*, 1933, **138** (6), 32.
[107] *Mitt. Kohlenforschungsinst. Prag.*, 1932 (4), 198; *Chem. Abs.*, 1933, **27**, 399.
[108] *Oil & Gas J.*, 1932, **31** (21), 14.
[109] *Oil & Gas J.*, 1932, **31** (23), 13.
[110] *Refiner*, 1933, **12**, 115, 174.
[111] *Refiner*, 1933, **12**, 110.
[112] *Refiner*, 1933, **12**, 180.
[113] *Oil & Gas J.*, 1932, **31** (32), 11.

vidual refinery has found the A.P.I. safety precautions only general, and takes elaborate care to control detailed safety work in the cracking plant by means of committees from the technical staff. A report outlining the fundamental safety factors in a cracking plant has been compiled by Marek,[114] who describes methods of inspection including external visual inspection, drill testing for corrosion, calipering, hammer testing, X-ray and hydrostatic pressure testing. Tight-wire measuring apparatus is recommended for determining wall thickness of reaction chambers. Hirsch[115] particularly notes the difficulties attending safety test-drilling for corrosion inspection.

Adams[116] reviews the numerous methods in use for combating corrosion in refineries, emphasising particularly resistant metals and alloys for the equipment. The trend in choice of metals for high temperature service, especially cracking tubes, is reported by Speller.[117] He recognises the need for knowledge of the effect of high temperature on the physical properties of these metals and recommends standardisation of procedure for creep testing. The present trend is thought to be toward wider use of alloy steels, especially 5 per cent. chromium type for corrosive crudes. Carbon steel is still used most generally. Addition of 1 per cent. tungsten or 0·5 per cent. molybdenum increases creep resistance. Very little 18 per cent. chromium—8 per cent. nickel alloy has been installed for cracking tubes this year, although it is admitted to justify added expense in some cases. Speller[118] has also reviewed the subject of alloy steels in refinery construction.

Another survey of alloy steels for petroleum refining equipment is presented by Smith,[119] who also takes particular note of the interrelation of the various metallurgical industries with the many branches of petroleum refining. He deals primarily with the preparation of the materials and fabrication of the high pressure, high temperature equipment. Newell[120] notes the increasingly wide choice of alloys and other corrosion resistant materials open to the refiner for his cracking coil tubes, while Fraser[121] deals specifically with the use of nickel and nickel alloys for this purpose.

A device for testing corrosion, described by Chapman,[122] was

[114] U.S. Bur. Mines, Tech. Paper 551, 1933.
[115] *Refiner*, 1933, **12**, 184.
[116] *Petr. Eng.*, 1933, **4** (8), 32.
[117] *Oil & Gas. J.*, 1933, **31** (39), 74.
[118] *Refiner*, 1933, **12**, 132.
[119] *Refiner*, 1933, **12**, 140.
[120] *Refiner*, 1933, **12**, 122.
[121] *Refiner*, 1933, **12**, 162.
[122] *Refiner*, 1933, **12**, 153.

designed as a means for exposing test specimens to gases or liquids in pressure vessels under operating conditions with minimum interruption of service.

XII. Reviews on Cracking.

General reviews on the subject of the cracking art have appeared in various languages for the information of people of various countries. The appearance of such general surveys is a strong indication of the growing expansion of cracking in many directions from its "homeland" in the United States.

In the United States, Nelson[123] reviews the state of knowledge of the cracking art at present, while Henny,[124] in England, discusses its recent developments in Europe. A survey of research progress in cracking in Japan has been made by Kobayashi.[125]

Cracking-process patents have been surveyed in Germany by Mayer,[126] while the theory of cracking as well as its industrial applications are reviewed in France by Grebel.[127] A brief outline of the principal industrial cracking-processes is also offered by Bourgault.[128] A similar series of brief descriptions of industrial cracking processes has been published in Russia by Valgis,[129] and another by Ginzburg.[130] The cracking of shale tars has been reviewed by Markovich.[131]

A book purporting to cover the vast field of cracking technology and chemistry has recently been published by Sachanen and Tilicheev,[132] and contains much of their own experimental data.

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[123] *Petr. Eng.*, 1933, **4** (11), 30.
[124] *Petr. Times*, 1933, **29**, 11.
[125] *J. Fuel Soc. Japan*, 1933, **12**, 436; *Chem. Abs.*, 1933, **27**, 3808.
[126] *Chem. Ztg.*, 1933, **57**, 81.
[127] *Génie Civil*, 1932, **101**, 317.
[128] *Arts et Métiers*, 1933, 169.
[129] *Aznefteizdat*, 1932, (32), 68; *Chem. Abs.*, 1933, **27**, 1152.
[130] *Aznefteizdat*, 1932, 44; *Chem. Abs.*, 1933, **27**, 1152.
[131] *Khom. Tverdogo Topliva*, 1931, **2** (11–12), 131; *Chem. Abs.*, 1933, **27**, 1741.
[132] Chemical Catalog Co. (1932).

Chemical and Physical Refining.

By C. G. Verver and R. N. J. Saal.

I. Chemical Refining.

Although it seems likely that the classical method of purifying petroleum products, by treatment with sulphuric acid, will continue to play a considerable part in petroleum technology for a long time to come, an ever-growing tendency to avoid its manifest disadvantages by employing other processes has been reported during the last few years. During the period now reviewed this trend has continued. It is probable, however, that the actual "flight from sulphuric acid refining" is not so rapid in practice as would appear from a study of the articles published, since these obviously deal with products presenting the greatest difficulties (*e.g.*, cracked spirit), whilst little change has, generally speaking, taken place in the well-established methods of treating such relatively "easy" materials as kerosines and white spirits.

Even in the case of cracked distillates, however, sulphuric acid refining still has its advocates. Trusty[1] argues that it possesses a number of good points, besides its disadvantages. The former are, as is well known, the considerable improvement in colour, gum, sulphur, odour and stability to light, whilst the latter include the high treating losses, the loss in knock-rating and the formation of oil-soluble acid reaction products. The loss in octane rating, consequent on all the operations connected with the acid-treating of Oklahoma, Kansas, and Arkansas Dubbs pressure distillates was investigated by Wirth, Kanhofer and Murphy,[2] and found to amount to a total of 2·5, 4·0 and 1·0 units in the order cited. Born[3] comes to the conclusion that most pressure distillates can be successfully refined with acid, with little loss in octane value, by a proper choice of conditions.

For the reduction of a high sulphur content, sulphuric acid is as yet in many cases the only suitable refining agent. During an investigation on Playa del Rey (California) crude oil, containing 2·2 per cent. of sulphur, Smith and Spangler[4] obtained the greatest diminution of sulphur in the straight-run gasoline, viz., 0·43 per cent. to 0·08 per cent., by a treatment with soda, 10 lb. of acid per barrel in three washes, followed by neutralisation and redistillation, whilst other refining agents (strong NaOH, $AlCl_3$, lime, cuprous oxide, Na_2CO_3 or oxidising agents) either failed to

[1] *Refiner*, 1932, **11**, 604, 605.
[2] *Oil & Gas J.*, 31.7.33, **32** (8), 13.
[3] *Nat. Petr. News*, 5.4.33, **25** (14), 23–28.
[4] *Oil & Gas J.*, 30.3.33, **31** (45), 75.

give the same reduction or resulted in a high ash content. In the case of another high-sulphur crude oil (Oregon Basin, Wyoming), Morell, Wirth and Strong[5] investigated various methods of refining the cracked gasoline; they concluded that treating methods involving a caustic (or plumbite) treatment and a water wash, drying, acid and soda (or plumbite) treatment may result in a reduction of acid consumption as against the more usual simple acid-caustic treatment. They also noted that it was preferable in this instance to treat fractions of the gasoline separately, rather than the entire distillate, owing to the unequal distribution of sulphur in various fractions.

In some cases it would appear, however, that sulphur reduction can readily be obtained without the use of sulphuric acid. Thus, it was found by Shipley[6] that the naphtha produced from Turner Valley crude (containing 0·15 to 0·19 per cent. of S.) could be treated to a sulphur percentage of 0·1 per cent. with caustic alone, and to 0·05 per cent. with the aid of sodium sulphide solution, whilst sulphuric acid (as well as hypochlorite, plubite and cupric chloride) treatments did not prevent gum formation or discoloration in daylight.

A useful laboratory method for a small scale continuous treatment of gasoline and other distillates with acid is described by Zublin,[7] who states that the results obtained by the batch treatment usually employed in the laboratory do not agree with those produced in continuous plant operation.

Various modifications of the normal sulphuric acid treatment are met with. Von Winkler,[8] for instance, describes the refining of gasoline obtained from Esthonian shale, and states that the yellow colour and unpleasant onion-like odour is not removed by sulphuric acid alone, but that these objectionable features may be eliminated by the addition of methanol, aldehydes, or other compounds to the acid. As usual, there are a number of patents[9,10,11,12,13,14] protecting various minor deviations from the normal procedure, either with respect to sulphuric acid treatment, or acid treatment coupled with adsorbents, etc. Gary[15] claims the process of refining lubricating oils by means of sulphur trioxide

[5] *Oil & Gas J.*, 20.7.33, **32** (9), 12.
[6] *Canad. J. Res.*, 1933, **8**, 119.
[7] *Oil & Gas J.*, 17.11.32, **31** (26), 74; *Refiner*, 1932, **11**, 558–559.
[8] *Chem. Z.*, 14.12.32, 991.
[9] E.P. 388,782, 28.2.33. Silica Gel Corp.
[10] U.S.P. 1,886,260, 1.11.32. E. B. Miller.
[11] U.S.P. 1,886,261, 1.11.32. E. B. Miller and G. C. Conolly.
[12] E.P. 395,635, 20.7.33. W. C. Holmes & Co., Ltd.
[13] U.S.P. 1,908,616, 9.5.33. E. Petty.
[14] U.S.P. 1,927,853, 26.9.33. C. W. Stratford.
[15] U.S.P. 1,893,138, 3.1.33. W. W. Gary.

diluted with liquid CO_2. Morell and Egloff[16] have protected the vapour-phase treatment of cracked distillates with SO_3 and steam in the presence of ferric sulphate. The acid refining of a lubricating oil, which has previously been submitted to oxidation, is the subject of a patent by Davis and Atkinson.[17]

The sulphonic acids formed on treating a petroleum product (principally a lubricating oil) with acid now find a steadily increasing use as emulsifiers, Twitchell reagents, etc. Von Pilat, Sereda and Szanowski[18] differentiate between α, β and γ sulphonic acids from mineral oils. The α and γ acids occur mainly or entirely in the acid tar; their calcium salts are respectively insoluble in ether and water, and insoluble in ether, but soluble in water. The β sulphonic acids are oil-soluble, whilst the Ca-salts dissolve in ether but not in water.

The disposal of acid tars is a perennial problem, their evaluation in the refinery by sweating and combustion is dealt with by Paginini[19]. "A new method for the regeneration of sulphuric acid from refinery acid sludge, known as the Hechenbleikner process, is described in two recent papers.[19a] It consists in decomposing the sludge in a rotary kiln by allowing it to flow in counter-current against hot combustion gases. The resulting gas, which may contain up to 20 per cent. of SO_2, is freed from volatile oil, and the greater part of the water vapour by passage through washers. After a final drying with 85–93 per cent. of sulphuric acid, the gas is diluted with air and contacted over a vanadium catalyst in the normal manner. It is claimed that 90 per cent. of the acid in the sludge is regenerated, the plant costs amounting to about $4 per ton of 100 per cent. acid. A coke of high heat value is obtained as a by-product from the kiln.

With regard to other well-established chemical refining agents, mention may first be made of a description by Greensfelder[20] of an apparatus in which the continuous neutralisation of acid-treated light oils may be controlled by means of a show glass and the constant addition of a suitable indicator solution, such as Methyl red or Xylenol blue. Wagner[21] (who incidentally gives a survey of the various methods of removing certain sulphur compounds, such as mercaptans and hydrogen sulphide, from gasoline) describes a continuous process of desulphurising gasoline with the aid of

[16] U.S.P. 1,897,582, 14.2.33.
[17] U.S.P. 1,927,823, 26.9.33.
[18] *Petr. Z.*, 18.1.33, **29** (3), 1–11.
[19] *Petr. Z.*, 30.8.33, **29** (34), 6–8.
[19a] Bartholomew, *Chem. Met. Eng.*, 1933, **40**, 642–645; Spangler, *Oil & Gas J.*, 26. 10.33, **32** (23), 76.
[20] *Petr. Z.*, 29.3.33, **29** (13), 6–8.
[21] *Oil & Gas J.*, 30.3.33, **31** (45), 38.

spent caustic soda solution (which by virtue of having absorbed hydrogen sulphide and free sulphur, contains polysulphides) and fresh soda solution. Day[22] claims the removal of gum-forming constituents from gasoline by treatment with an alkaline solution under pressure at 350–500° F. followed by redistillation. The separation of the acidic bodies from a spent soda solution is the subject of a patent by the Trinidad Leaseholds, Ltd., and Others,[23] who employ hydrogen sulphide, assisted by sulphuric acid, followed by an extraction with petroleum spirit.

Some attention has been devoted to the neutralisation of acid-treated oils, and the removal of acidic bodies generally, with other alkalies besides caustic soda. Lachmann[24] treats gasoline vapours with steam under pressure and calcium carbonate. Hydrogen sulphide, as is shown by another author,[25] may be removed from corrosive vapours by passing them through a mist of saturated lime water. The neutralisation of an acid-treated oil by means of moist magnesium oxide is covered in a patent by Caldwell.[26]

The "sweetening" of a gasoline involves the conversion of the mercaptans into dialkyl-disulphides, and the processes employed to effect this change may be subdivided into: (*a*) reactions involving the addition of an atom of sulphur, and (*b*) oxidation reactions. The former group is, of course, represented by the well-known doctor treatment, and this reaction has this year again brought forth a crop of patents, usually covering minor variations in the standard procedure. Whereas the lead mercaptides remaining dissolved in the oil upon treatment with plumbite solution are usually decomposed with sulphur, two other methods are described for effecting the conversion, the first involving an oxidation with $KMnO_4$,[27] the second with a solution of a hypochlorite.[28] Morell[29] claims that the lead mercaptides may be precipitated by exposure to ultra-violet light.

A number of patents deal with a contact treatment of gasoline with lead oxide in the liquid or in the vapour-phase, with or without the addition of adsorbents or other refining agents, such as alkalies.[30,31,32,33,34]

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[22] U.S.P. 1,902,221, 21.3.33.
[23] E.P. 386,977, 18.1.33.
[24] U.S.P. 1,914,668, 20.6.33.
[25] Anon., *Refiner*, 1933, **12**, 50.
[26] U.S.P. 1,921,116, 8.8.33.
[27] Behrens, U.S.P. 1,927,147, 19.9.33.
[28] McClaughry and Moore, U.S.P. 1,927,068, 19.9.33.
[29] U.S.P. 1,904,382, 18.4.33.
[30] Darrow, U.S.P. 1,903,094, 28.3.33.
[31] Morell, U.S.P. 1,904,382, 18.4.33.
[32] Hirt, U.S.P. 1,910,288, 23.5.33.
[33] Cannon, U.S.P. 1,924,911, 29.8.33.
[34] Cannon, U.S.P. 1,926,226, 19.9.33.

The treatment of a gasoline with a solution of an alkali sulphide is dealt with in a patent by Malisoff[35]; its use has already been referred to in connection with the work of Shipley on Turner Valley crude.[36]

A reagent with a sweetening action somewhat analogous to that of litharge is Brucite ($Mg\,OH_2$), which reacts with mercaptans to form magnesium marcaptides; the latter are decomposed by sulphur to magnesium sulphide. This compound after some time forms a film covering the surface of the Brucite (which is packed into a tower), so that periodic revivication with boiling water, soda and water, followed by drying, is necessary.[37]

Oxidative reagents are represented in the first place by hypochlorite solutions; it would appear that three-fourths of the (American) natural gasoline is refined in this manner.[38] The effect of the composition and temperatures of the hypochlorite treating solutions is described by Ritchie,[39] who particularly draws attention to the increase in chlorine consumption with rising temperature.

Another sweetening agent depending on an oxidative reaction is a cupric salt. Morell[40] has patented the use of a solid reagent consisting of a copper salt, a hydroxide of an alkali metal, an alkaline earth oxide and a solid adsorbent. A refining process in which a copper halide is combined with phosphorus pentoxide is proposed by Malishev,[41] whose introduction of the latter reagent created some interest last year. A somewhat different use of copper is described by Von Fuchs,[42] who employed the oxide or precipitated metal (which is stated to convert the mercaptans into copper mercaptides) for treating straight-run or cracked spirits, the spirit being finally refined with sulphuric acid (strong or fuming) and 58 per cent. ferric chloride, the latter acting as the necessary oxidising agent. Amongst the other refining methods met with in last year's literature there are several which presumably rely upon oxidation; alkali ferricyanides (for cracked fuel, followed by acid treatment, neutralisation and redistillation)[43], ozonised air (followed by H_2SO_4, $FeCl_3$ or $Fe_2(SO_4)_3$, neutralisation and redistillation,[44] oxygen in the vapour-phase at 300–350° F.[45],

[35] U.S.P. 1,899,042, 28.2.33.
[36] *Canad. J. Res.*, 1933, **8**, 119.
[37] Higgins, *Nat. Petr. News*, 12.4.33, **25** (15), 26–31.
[38] Anon., *Refiner*, 1933, **12**, 278–280.
[39] *Petr. Eng.*, Sept., 1933, **4** (8), 28.
[40] U.S.P. 1,911,640, 30.5.33.
[41] U.S.P. 1,914,953, 20.6.33.
[42] *Petr. Z.*, 1933, **29** (11), 5–8.
[43] Heath, U.S.P. 1,888,382, 22.11.32.
[44] Improved Hydro-Carbon Processes; E.P. 387,447, 9.2.33.
[45] Yonker, U.S.P. 1,910,734, 23.5.33.

oxygen under the influence of X-rays,[46] an aqueous iodine solution (for treating cracked spirits in the vapour-phase),[47] and an aqueous perborate solution.[48]

In the past, two reactive metallic halides have acquired some fame for the refining of petroleum products. Aluminium chloride—the use of which, for treating purposes, is principally coupled with the name of the Gulf Refining Co.—again figures in a patent granted to the same concern,[49] which covers its use at temperatures below 150° C. in the presence of an excess of chlorine. Considerable interest is being displayed, principally in America, in the Lachmann process, employing zinc chloride. Albright[50] describes the application of this treating method in conjunction with a Winkler-Koch skimming and cracking unit, and reports 98 per cent. recovery of cracked spirit, the refined material having a colour of 30 plus Saybolt, and showing no drop in octane number with respect to the unrefined spirit. The use of $ZnCl_2$ in conjunction with ammonium chloride is the subject of a patent by Kimball,[51] whilst several patents would seem to aim at a similar effect by specifying the combined use of hydrochloric acid and zinc (or other metals), either at atmospheric or increased pressures.[52,53,54,55]

A novel refining agent for petroleum products is anhydrous hydrofluoric acid, which, as in the case of sulphuric acid, converts unsaturated hydrocarbons into insoluble polymers.[56] On account of its low boiling point (19·4° C.) it is readily removed from the oil, but it suffers from manifest disadvantages, owing to its corrosive and poisonous nature and its high price.

Not more than passing mention can be made of the remaining chemical refining agents encountered during the past year. Alkali (and other) metals were again the subject of two investigations[57,58] and a patent.[59] For vapour-phase refining, mainly of cracked spirits, the use of borax (with or without absorbent clay and steam[60,61]) of an aqueous solution of calcium and magnesium

[46] Meckler, U.S.P. 1,897,617,14.2.33.
[47] Oberle, U.S.P. 1,893,438, 3.1.33.
[48] Morell, U.S.P. 1,927,182, 19.9.33.
[49] E.P. 398,032, 7.7.33.
[50] *Refiner*, 1933, **12**, 298–309.
[51] U.S.P. 1,917,648, 11.7.33.
[52] Day, U.S.P. 1,920,247, 1.8.33.
[53] Day, U.S.P. 1,920,248, 1.8.33.
[54] Morell, U.S.P. 1,920,270, 1.8.33.
[55] Univ. Oil Prods. Co. and A. L. Mond, E.P. 395,448, 20.7.33.
[56] Lederer, *Erdöl u. Teer*, 1933, **9**, 107–108.
[57] Hofmeier and Wisselinck, *Brenn.-Chem.*, 1933, **14**, 286–288.
[58] Dittrich, *Brenn.-Chem.*, 1933, **14**, 283–284.
[59] Magill, U.S.P. 1,890,881, 13.12.32.
[60] Morell and Essex, U.S.P. 1,890,229, 6.12.32.
[61] Morell and Essex, U.S.P. 1,890,230, 6.12.32.

chlorides at 300° F.[62] of a solution of beryllium and ammonium chlorides,[63] of " Minette " (iron ore) in the presence of hydrogen[64] and of the chromite of a metal (Cu or Cd), likewise in an atmosphere of hydrogen,[65] are described. For sweetening, gum removal, and sulphur reduction purposes, a solution of a cadmium-ammonia compound containing an excess of ammonia,[66] an acid solution of the chlorite of an alkali metal,[67] a mixed base oxychloride (*e.g.*, of zinc and lead),[68] and an alkaline solution of a naphthenic acid soap at 212–300° F. are advocated.[69]

Methods for the catalytic removal of sulphur from spirits by passing the vapours over metallic sulphides are, of course, well known, but a publication has appeared during the last year demonstrating that the efficiency of the catalyst (*e.g.*, cupric sulphide) may be greatly enhanced by employing silica gel as a support.[70]

Before leaving the subject of chemical refining, some articles dealing more generally with the necessity or the effects of such a treatment may be mentioned. The fact that super-refined oils are in some respects more unstable towards oxygen than their less drastically treated equivalents has long been known, and Typke[71] has shown that white oils possessing a relatively high tar number can be improved from this point of view by the addition of a less refined oil, or of an (aromatic) extract obtained from such an oil with a selective solvent such as methanol, acetone or SO_2. Gray[72] has investigated various methods of refining the petroleum fractions used for spray oils, and concludes that the substances injurious to plants can best be removed by filtration over various media, sulphonation or alcoholic extraction. The reversion of the colour of refined lubricating oils prepared from a Burmah crude by different means (*e.g.*, with and without vacuum) with the aid of acid, SO_2 and earth treatments, was studied by Bowen[73] under varying conditions of light and heat. Danaila and Boltus Goruneanu[74] have shown that the use of a high vacuum alone is not sufficient to yield good transformer oils from Roumanian

[62] Kimball, U.S.P. 1,892,801,3.1.33.
[63] Rostin, U.S.P. 1,904,172, 18.4.33.
[64] Kimball, U.S.P., 1,895,223, 24.1.33.
[65] Smith, U.S.P. 1,889,388, 29.11.32.
[66] Culmer, U.S.P. 1,899,314, 28.2.33.
[67] Taylor, U.S.P. 1,908,273, 9.5.33.
[68] Sumpter, U.S.P. 1,912,603.
[69] Stratford, U.S.P. 1,904,173, 18.4.33.
[70] Holmes, Elder and Beeman, *J. Phys. Chem.*, 1932, **36**, 2981.
[71] *Erdöl u. Teer*, 1933, **9**, 29.
[72] *Oil & Gas J.*, 2.2.33, **31** (37), 8.
[73] *J. Inst. Petr. Techn.*, 1933, **19**, 364–375.
[74] *Petr. Z.*, 9.11.32, **28** (45); *Motorenbetrieb*, **5** (11), 4–7.

(Moreni) crude, but that it must be supplemented by an acid treatment.

A number of articles and patents dealing with the regeneration of used oils have appeared during the last year and are referred to below.[75]

II. Physical Refining.

(*a*) Extraction processes.
(*b*) Dewaxing processes.
(*c*) Absorption processes.
(*d*) Distillation. (This subject is dealt with in another review).

Whilst it will be evident from the preceding section that chemical refining, though subject to a steady development during the past year, has not undergone any very startling change, it may safely be said that physical refining is at the time of writing passing through a " boom " period. This is especially true with regard to the first two of the sub-sections mentioned above, which just now occupy a major amount of the space in the technical petroleum press.

(*a*) *Extraction.*—The extraordinary interest displayed in the extraction of lubricating oils at the present time appears strange, at first sight, since the Edeleanu treatment was introduced more than 25 years ago, and a plant for the SO_2-extraction of light lubricating oils has been in operation in Europe for approximately 11 years. The sudden hold which these methods have obtained on the technology of mineral oils, principally in America, is probably indirectly due to the development in the production of hydrogenated and synthetic lubricants during the last few years. The interest of technical men thereby became centred on such properties of lubricating oils as the viscosity-temperature slope, the Conradson Carbon figure and the resistance to sludging, whilst it became evident that these factors to a large degree depended on a certain group of hydrocarbons (*i.e.*, those containing aromatic rings) and that by their elimination or chemical conversion the characteristics of the material could be profoundly altered. (It may be mentioned, in passing, that American authors with very few exceptions refer to the extractable part of an oil as the " naphthenic " fraction and the insoluble part as the " paraffins," although there is little doubt that the essential difference is constituted by the presence or absence of unsaturated rings in the molecule. The confusion existing in this respect and in such matters as the expression of the

[75] Mayo, E.P. 383,081 ; Hook, *J.S.A.E.*, 1933, **32**, 20 ; Mockler, *Oil & Gas J.*, 15.12.32, **31** (30), 28 ; Stormonth, U.S.P. 1,903,370 ; Maverick and Matheson, U.S.P. 1,914,999 ; Ambler, U.S.P. 1,926,188 ; Fox, U.S.P. 1,930,006.

characteristics of the oil as a " Viscosity Index " or a " Viscosity-Gravity-constant " was discussed at the World Petroleum Congress in a paper by Mayer.[76])

Of the many solvents at present competing in the field of lubricating oil extraction, the following may be cited as having quite or nearly reached the stage of technical application :—

(i) Nitrobenzene.[77]
(ii) Sulphur dioxide–benzole.[78]
(iii) Phenol.[79]
(iv) Chlorex (β-β^1-dichloro ethyl ether).[80]
(v) Furfural.[81]
(vi) Cresol–propane (" Duo-Sol " process).[82]
(vii) Crotonaldehyde.[83]

Besides these solvents, the following are mentioned in patents and in last year's literature :—

Furfuryl alcohol.[84]
Benzonitrile.[85]
Benzaldehyde.[86]
Cresol.[87]
Wood tar acids.[88]
Ethylene glycol ethers and derivatives.[89]
Acetone.[90]

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[76] Mayer, *Proc. World Petr. Cong.*, 1933, **2**, 375.
[77] Ferris and Houghton, *Refiner*, 1932, **11**, 560 ; *Refiner*, 1933, **12**, 318 ; *Proc. World Petr. Congr.*, 1933, **2**, 370 ; *Refiner*, 1933, **12**, 435.
[78] Buchel and Saal, D.R.P. 517,712 ; Cottrell, *Oil & Gas J.*, 1932, **31** (28), 10 ; *Proc. A.P.I.*, 1933, **14** (3), 60 ; *Refiner*, 1933, **12**, 432.
[79] Stratford, Moor and Pokorny, *Nat. Petr. News*, 1933, **25** (13), 17 ; *Proc. World Petr. Congr.*, 1933, **2**, 362. ; Stratford, Pokorny and Huggett, *Proc. A.P.I.*, 1933, **14** (3), 90 ; *Refiner*, 1933, **12**, 458.
[80] Foster, *Nat. Petr. News*, 1933, **25** (33), 35 ; Bage, Büchler and Diggs, *Nat. Petr. News*, 1933, **25** (14), 35 ; *Ind. Eng. Chem.*, 1933, **25**, 418 ; *Oil & Gas J.*, 1933, **31** (48), 14 ; Bahlke, Brown and Diwoky, *Proc. A.P.I.*, 1933, **14** (3), 77 ; *Refiner*, 1933, **12**, 445 ; *Oil & Gas J.*, 1933, **32** (23), 60 ; Foster, *Nat. Petr. News*, 1933, **25** (34), 34.
[81] Eichwald, U.S.P. 1,550,523 ; Marly, MacCarty and Gross, *Proc. A.P.I.*, 1933, **14** (3), 47 ; *Refiner*, 1933, **12**, 430 ; *Nat. Petr. News*, 1933, **25** (43), 26 ; *Oil & Gas J.*, 1933, **32** (23), 78.
[82] Bataafsche Petroleum Maatschappij, D.R.P. 539,831 ; Tuttle and Max B. Miller, *Proc. A.P.I.*, 1933, **14** (3), 85 ; *Refiner*, 1933, **12**, 453 ; Max B. Miller, *Nat. Petr. News*, 1933, **25** (41), 26.
[83] Poole and Wadsworth, *Proc. A.P.I.*, 1933, **14** (2), 39 ; *Refiner*, 1933, **12**, 412 ; Poole, *Nat. Petr. News*, 1933, **25** (33), 28 ; *Oil & Gas J.*, 1933, **32** (23), 49.
[84] Hill, U.S.P. 1,883,374.
[85] Kurtz, U.S.P. 1,899,969 ; Atlantic Ref. Co., E.P. 383,801.
[86] Birkhimer, U.S.P. 1,904,402.
[87] Tuttle, U.S.P. 1,912,349.
[88] Tuttle, U.S.P. 1,912,348.
[89] Henderson, U.S.P. 1,908,018.
[90] U.S.P. 1,920,125.

Acrolein.[91]

Aliphatic aldehyde mixtures (Propionic aldehyde).[92]

Mixtures of phenol and polyhydric alcohols.[93]

No details are, however, to be found with regard to their technical use, their advantages and disadvantages. As yet it is even not possible to effect a definite comparison between the results obtained with the solvents mentioned in the first list, since very few comparable data are as yet available, whilst the solvent power and selectivity of the media change between large limits with varying proportions and temperatures. The following general remarks will, therefore, have to suffice for the present.

(i) *Nitrobenzene*.—This process has been developed by the Atlantic Refining Co. Nitrobenzene is very selective with respect to unsaturated versus saturated compounds, and it shows little or no selectivity as regards light *v.* heavy hydrocarbons. The solvent power is fairly high, and it is consequently always necessary to operate at relatively low temperatures. The disadvantage of its toxicity would appear to be surmountable.

(ii) *SO_2-benzol*.—Patented by Buchel and Saal (Bataafsche Petroleum Maatschappij). This solvent is now technically used by the Edeleanu Company. It is an outcome of the fact that SO_2 alone has too low a solvent power at the normal temperatures at which it is used. The solvent power of SO_2 is greatly increased by admixture of benzol; the process thereby obtains a very considerable flexibility.

(iii) *Phenol* (Imperial Oil Refineries).—Phenol has already been employed on a technical scale for several years.

(iv) *Chlorex* (Standard Oil, Indiana).—One of the specific advantages of this solvent would appear to be its high specific gravity, which promotes a rapid separation of the raffinate and extract layers.

(v) *Furfural*.—This solvent, discovered by Eichwald (Bataafsche Petroleum Maatschappij), is now employed by the Texas Company. Owing to the high temperatures at which it is best applied, its use in a continuous counter-current extraction tower, preferably employing a temperature gradient, is possible.

(vi) *Cresol–Propane* (technically developed by Max B. Miller & Co.).—This method known as the "Duo-Sol" process relies upon the demixing of a pair of solvents, which in combination have specific solvent powers for the unsaturated and saturated components of the oil respectively. (The basic patent for this principle was taken out by the Bataafsche Petroleum Maatschappij).

[91] Poole and Wadsworth, *Refiner*, 1933, **12**, 412.
[92] Birkhimer, U.S.P. 1,910,422.
[93] Stratford, U.S.P. 1,892,655.

The use of propane naturally entails a closed system, operating under pressure.

(vii) *Crotonaldehyde.*—This solvent is being developed by the Foster Wheeler Company, which also possess the rights over the use of acrolein. For the separation of extract and raffinate layers centrifuging is made use of.

In general it may be said that the raffinate obtained by these processes—at all events if a lubricating oil distillate is the base material—only need a clay treatment in order to bring them to the required colour. The stability of all of the solvents mentioned appears to be sufficient, though it is necessary to exclude oxygen in the case of the less resistant media.

Other developments worthy of mention are some modifications of the Edeleanu process, consisting in the addition of clay to the raffinate before distilling off the SO_2,[94] and in the extraction of a total distillate to 400° C. before a separation into fractions is undertaken.[95] Patent literature further mentions the combined use of nitrobenzene and sulphuric acid,[96] and the use of nitrobenzene, specifically for the preparation of insulating oils.[97]

Another process, which is also attracting considerable interest in America, is the deasphaltisation of oils by means of liquid propane (or still lighter hydrocarbons).[98] This must also be classified under the heading of the extraction methods, though radically different from what is usually understood by the term. Whilst the extraction solvents mentioned previously are designed to differentiate between saturated and unsaturated hydrocarbons, the propane process relies upon the different solvent power for hydrocarbons (more especially those of aromatic character) with a high and low molecular weight. By solution in propane under pressure at normal temperatures the "asphaltic bodies" are precipitated as a solid or highly viscous mass, whilst the light-coloured hydrocarbons remain in solution. It is obvious that this process can very readily be combined with the cresol-propane extraction process mentioned above, and, also, with the propane dewaxing method to be discussed later.

With regard to the more general aspects of extraction processes, reference may finally be made to a theoretical discussion of extraction principles[99] and of a calculation of the number of stages

[94] Lazar, U.S.P. 1,885,524.
[95] Rosenberg, U.S.P. 1,908,646.
[96] Sinclair Ref. Co., E.P. 390,697.
[97] Atlantic Ref. Co., E.P. 394,404.
[98] "Metan" spolka z ograniczona odpowiedzialnoseia, D.R.P. 362,458; Union Oil Company of California, French Patent, 740,803; I. G. Farbenind., E.P. 389, 113; Bray, Swift and Carr, *Oil & Gas J.*, 1933, **32** (24), 14.
[99] Hunter and Nash, *Proc. World Petr. Congr.*, 1933, **2**, 340.

necessary for separating a binary liquid mixture by extraction (as analogous to distillation).[100]

(*b*) *Dewaxing.*—As already stated, methods for dewaxing lubricating oils are at present passing through a period of lively progress. The following technically developed processes have, during the past year, been advocated for the purpose :—

(i) Dewaxing by means of propane.[101]
(ii) Dewaxing by means of benzol-acetone.[102]
(iii) Dewaxing by means of trichloro-ethylene.[103]
(iv) Dewaxing by the use of a " filter aid."[104]

(i) *Dewaxing with Propane.*—Dewaxing with propane will almost invariably be coupled with a preliminary deasphaltisation by means of the same solvent (see *ante*). The light coloured oil from which the asphaltic material has been precipitated is chilled by self-refrigeration and the wax removed by filtration.

(ii) *Dewaxing with Benzole Acetone.* (Indian Refining Co.).—This method has been in use since 1927 ; it employs a mixture, usually consisting of two parts of benzol to one part of acetone, as a solvent, followed by refrigeration and filtration along normal lines. It is apparent that an extraction with acetone can conveniently be employed prior to this dewaxing process.

(iii) *Trichloro-ethylene.*—The use of this solvent, which has been developed by the Separator Nobel Co., later by the Standard Oil Development Co., has already been described last year. It is characterised by the unusual feature that the wax is lighter than the mother liquor so that, in the centrifugal separation employed, the wax is removed from the *inside* of the system ; furthermore, the success of the method is not dependent on the specific gravity of the wax.

(iv) *Dewaxing with Filter Aids.*—Dewaxing processes relying on the decreased resistance to filtration of paraffin wax in oil diluted with a solvent when in the presence of a voluminous powder, have of course, been in use for a number of years ; the Weir process is one of the best-known forms of such a method. Diatomaceous earth now appears to be one of the principal filter-aids employed in this process.

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[100] Saal and van Dijck, *Proc. World Petr. Congr.*, 1933, **2**, 352.

[101] Bahlke, Giles and Adams, *Proc. A.P.I.*, 1933, **14M** (3), 16 ; *Refiner*, 1933, **12**, 229 ; Conine, *Oil & Gas J.*, 1933, **31** (50), 11 ; Shell Petroleum Corporation, U.S.P. 1,755,810, 1,713,888.

[102] Govers and Bryant, *Proc. A.P.I.*, 1933, **14M** (3), 7 ; *Refiner*, 1933, **12**, 224 ; Foster, *Nat. Petr. News*, 1933, **25** (34), 36 ; Govers, U.S.P. 1,920,125 ; Anderson, U.S.P. 1,907,703.

[103] Pester, *Proc. A.P.I.*, 1933, **14M** (3), 4 ; *Refiner*, 1933, **12**, 235 ; *Oil & Gas J.*, 1933, **32** (1), 52 ; Backlund, *J. Inst. Petr. Techn.*, 1933, **19**, 1.

[104] Gee, *Proc. A.P.I.*, 1933, **14M** (3), 24 ; *Refiner*, 1933, **12**, 238 ; Brady, *Petr. Eng.*, 1933, **4** (5), 35 ; Lyons, U.S.P. 1,920,922 ; Manlay, U.S.P. 1,892,283.

To assist the removal of slop-wax from a lubricating oil, Lowery[105] proposes the addition of small quantities of petrolatum before chilling and centrifuging; Hendriksen has patented a similar addition of a colloidal asphaltite (Grahamite).[106] Methylene chloride and esters are advocated for dewaxing purposes by Carlisle and Levine.[107] Dichlorethane has been patented with the same object by Jones,[108] but little data are as yet to hand about these solvents.

Researches which are of interest to students of the above problems were published by Poole and Mangelsdorf[109] and Walikowsky and Lykow[110] who devoted their attention to the solubility of petroleum waxes and oils in various solvents. Studies on filtration were carried out by Ruth, Montillon and Montonna.[111] An interesting account of laboratory methods for controlling plant dewaxing has been given by Davis and Campbell.[112] The tests employed by these authors include determinations of viscosity, distillation range and wax content and an examination of the wax crystal structure by means of a microscope fitted with a water-jacketed hot stage. A discovery of special interest is the subject of a patent granted to Anderson,[113] who found that when a waxy petroleum fraction of narrow boiling range is admixed with a wax fraction of another boiling range, the latter partially or wholly displaces the wax originally dissolved. After filtration it is therefore possible to effect a separation of wax and oil by a simple fractional distillation. Peterkin and Smith have been granted a patent for a dewaxing process employing solutions of alkaline silicates, which are stated to lower the surface tension between oil and wax and thereby to facilitate the process of separation.[114]

(c) *Adsorption.*—Refining by contact with adsorbents is seldom dependent on a physical action alone, as it is usually accompanied by various chemical processes such as polymerisation, cracking, etc. It is, however, convenient to deal with the various refining processes relying mainly on the use of adsorbent materials under a single heading. Since it would appear that few fundamental changes have taken place in this field, a brief mention of the more salient points encountered in the technical and patent literature will be sufficient.

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[105] U.S.P. 1,886,344.
[106] U.S.P. 1,901,240.
[107] *Ind. Eng. Chem.*, 1932, **24**, 384; see also Sullivan and Adams, U.S.P. 1,917,910.
[108] U.S.P. 1,930,479.
[109] *Ind. Eng. Chem.*, 1932, **24**, 1215.
[110] *Petr. Ind.* (*Russ.*), 1933, **24**, 123.
[111] *Ind. Eng. Chem.*, 1933, **25**, 76, 153.
[112] *Oil & Gas J.*, 25.5.33, **32** (1), 49.
[113] U.S.P. 1,927,051.
[114] U.S.P. 1,929,933; U.S.P. 1,929,934.

Nutting[115] has published a number of reports dealing with different kinds of bleaching clays, their activity, suitability for regeneration, filtration characteristics, the stability which they confer to the oil, etc. Frescott gives a similar review on the subject of contact treating clays.[116] The relative merit of a large number of adsorbents has been compared by Dubrisay,[117] whilst the effect of the time of lubricating oil treatment with clay at elevated temperatures has been discussed by Kalichevsky and Ramsay.[118] The selective adsorption of the aromatic constituents of benzine by means of silica gel is encountered in a publication by Hofmeister and Meiner.[119]

A naturally active bleaching clay, which in view of its low price would appear to present interesting possibilities in spite of its rather limited decolorising efficiency, has been found in "Carlonite," a mineral occurring in the Carlsbad region.[120]

It is not possible to do more than refer to the large number of patents dealing with the refining of spirits with the aid of adsorbents. Most of these are variations of the well-known processes making use of the polymerising action of active earths on cracked gasolines in the vapour phase, or in a combination of liquid and vapour phases.[121-128]

A description of a continuous method of treating cracked gasoline in the vapour phase with a suspension of clay in a carrier liquid, as employed in several Canadian refineries, has been published by Willson.[129]

With regard to the treatment of petroleum products with adsorbents in the liquid phase, Lachmann[130] has protected the process of sweetening motor spirit with an aqueous solution of an alkali salt (pH greater than 7·4) containing active charcoal. Watson has patented a treatment of gasoline in the liquid phase with

[115] *Ind. Eng. Chem.* (*Anal.*), 1932, **4**, 139; *Refiner*, 1932, **11**, 286: *Refiner*, 1933, **12**, 80.
[116] *Petr. Eng.*, 1933, **4** (12), 44.
[117] *Ann. des Comb. Liq.*, 1933, **8**, 607.
[118] *Ind. Eng. Chem.*, 1933, **25**, 941.
[119] *Z. Angew. Chem.*, 1933, **46**, 229.
[120] Belani, *Petr. Z.*, 14.12.32, **28** (50), 11–12; Fussteig, *Matt. Grasses*, 15.2.33 (298), 9752–54.
[121] Moore, U.S.P. 1,887,941.
[122] Osterstrom, U.S.P. 1,891,106–9.
[123] Miller, U.S.P. 1,895,081.
[124] Osterstrom, U.S.P. 1,897,328.
[125] Gray, U.S.P. 1,908,599.
[126] Herthel, U.S.P. 1,908,606.
[127] Brown, U.S.P. 1,930,453.
[128] Hall and Grahame, U.S.P. 1,930,974.
[129] *Oil and Gas J.*, 30.2.33, **31** (45), 61.
[130] U.S.P. 1,890,516.

fuller's earth, in a pipe heater under pressure,[131] whilst another patent of similar bearing has appeared under the name of Weaver.[132]

The thin-film evaporation of lubricating oils is combined with clay contacting by Darlington[133]; other patents which have made their appearance in the subject of the clay treatment of lubricating oils are referred to below.[134-139]

Finally, mention may be made of a description by Zublin[140] of methods used for the recovery of refinery contact clays. These methods comprise: washing and burning (generally to a temperature of 900–1000° F.) and solvent extraction. The efficiency of these methods and the procedure followed varies with different clays and even with the lubricating oil with which the clay has been used.

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[131] U.S.P. 1,894,331.
[132] U.S.P. 1,929,861.
[133] U.S.P. 1,888,346.
[134] Osterstrom, U.S.P. 1,894,323.
[135] Hoover, U.S.P. 1,896,583.
[136] Baylis and Bilden, U.S.P. 1,898,165.
[137] Bilden, U.S.P. 1,898,168.
[138] Baylis, U.S.P. 1,906,356.
[139] Ebaugh, U.S.P. 1,906,951.
[140] *Oil & Gas J.*, 27.10.32, **31** (23), 12.

Natural Gas and Natural Gasoline.

By Miss THELMA HOFFMANN.

NATURAL GAS.

THE production of natural gas in 1932 continued the downward trend begun in 1931, production being 8 per cent. lower than the year before[1] :—

1932.	
Production	1,555,990,000,000 cu. ft.
Consumption (prod. plus imports minus exports) ..	1,554,335,000,000 cu. ft.
,, for field purposes	529,378,000,000 (34%)
,, ,, domestic and commercial ..	385,887,000,000 (25%)
,, ,, manufacture of carbon black ..	168,237,000,000 (11%)
,, ,, electric, public utility, power plants	107,239,000,000 (7%)
,, ,, used at petroleum refineries ..	67,467,000,000 (4%)
,, ,, other industrial uses	296,127,000,000 (19%)

This decrease in consumption was caused by the smaller demand for industrial purposes.. Domestic and commercial use of natural gas continued to advance with a 1 per cent. increase in the number of customers served. The average price continued to rise from 65·3c. per thousand cu. ft. in 1931 to 69·3c. in 1932.

While the statistics for 1933 are not complete, the preliminary figures show an increased consumption over 1932, probably of about 1 per cent. A small decline in sales for domestic and commercial purposes was shown, with a slight decrease in the number of customers. The amount for industrial purposes showed an increase of about 7 per cent. over the 1932 figures. The amount of gas used for field operations remains about the same.[2]

Natural gas pipeline construction in 1932 was at a low ebb with only short lines being built. There was little, if any, increase in 1933.

The problem of soil corrosion of pipe lines has received a great deal of attention in the last few years. Oil companies, gas companies and the Bureau of Standards have all studied the various phases of this problem. In March and April of 1933, the Bureau of Standards held a conference on soil corrosion in both Washington, D.C., and Los Angeles, California. At this conference nearly 50 papers were presented and discussed, covering the many important points such as soil surveys and the most satisfactory method of conducting them, causes of corrosion, types of protective covering, etc.[3] Copper in very thin sheets has been recommended for pipe protection. Its advantage lies in the fact that the surface

[1] *Bureau of Mines*, M.M.S., 234.
[2] *Oil & Gas J.*, 11.1.34, **32** (34), 69.
[3] *Western Gas*, **9**, No. 5, pp. 14–19.

is tough, smooth, impervious to moisture and corrosion resistant. The copper wrapping, being a good conductor, would prevent stray currents from reaching the pipe.[4] These currents in the soil call for a new type of survey in addition to the general soil survey for corrosivity. Cathodic pipe protection has been used to some extent to combat these conditions. It has been found that in short pipes, as in a city net work, the corrosivity in the soil is the dominating factor in the life of a pipe, while in long continuous lines the soil currents are more important.[5]

Finding leaks in a gas line and repairing them is always a problem. In city areas, testing a line for leaks is more complicated than in the transmission lines in open country where gas under pressure is used. Because of the safety factor, hydraulic testing is being used in congested districts.[6] A new device called a Soundograph has been developed for detecting leaks. It is based on the principle of amplifying sound set up in the interior of a pipe by a leak. Through measuring the intensity of the sound in different positions, the leak can be located.[7]

While natural gas from most districts does not have H_2S as an impurity, it does occur in the gas from some of the Texas fields. Recent developments in purifying natural gas include the removal of H_2S by using a mixture of di- and tri-ethanolamine, removal by means of soda ash and by washing out the H_2S by sodium phenolate solution.[8]

Natural Gas Studies of the Bureau of Mines.

The U.S. Bureau of Mines has been carrying on important work in matters relating to petroleum and the natural gas industry. A recent Bureau of Mines paper contains its history and a summary of its work, past and present.[9] One of its more recent projects was the determination of the viscosity of natural gas under varying conditions. The existing methods of determining viscosity of gases being unsuitable for their purpose, Berwald and Johnson devised a very simple method. Results obtained by their apparatus checked very well with existing figures. Viscosity determinations at 60° F. at atmospheric pressure were made of 25 samples of natural gas of different compositions and a variation of about 25 per cent. was found. This was to be expected, as the composition of the gas samples varied greatly. Determinations were made

[4] *Oil & Gas J.*, 29.9.32, **31** (19), 63.
[5] *Western Gas*, **9** (4), 20–23.
[6] *Western Gas*, **9** (12), 12–13.
[7] *Gas Age Record*, **71**, 381–3.
[8] *Chem. & Met. Eng.*, 1933, **40**, 290.
[9] *U.S. Bureau of Mines I.C.*, 6737.

at different temperatures and pressures, the temperature affecting the viscosity and the pressure showing very little effect.[10]

As natural gas is often measured and transported under high pressure, the problem of deviation from Boyle's Law arises. This law holds for natural gas only at low pressures. It is estimated that the application of the deviation factor to field gas sales in California alone increases the meter volume between 275 and 300 million cu. ft. This correcting of pressure volume relations is an important consideration in all operations carried out at higher pressures, as repressuring, solving of high pressure problems on absorption, rectification, etc. The deviation is influenced by the composition of the gas, the heavier components showing greater deviation than the lighter ones. Temperature also affects deviation, an increase in temperature causing a decrease in the correction factor. It is believed that a relationship may be established between specific gravity and deviation. This work, however, has not been completed.[11, 12]

Another Bureau of Mines study has been made on the solubility and liberation of gas from natural oil-gas solutions. Shrinkage effects and change in gravity of the oil were observed. Pressure and temperature, of course, have marked effects. Tables and graphs are given for the solubility of hydrocarbon gases in different crude oils.[13] A similar study has also been made in Russia on the solubility of hydrogen and natural gas in oils at high operating temperatures and pressures.[14]

The limits of inflammability of natural gas have been studied. This subject was investigated for the pure components of natural gas as well as for the gas itself. Tables and curves prepared give these limits with varying amounts of nitrogen and carbon dioxide. Studies were made on the extinction of propane and butane flames by the addition of nitrogen and carbon dioxide.[15, 16]

Water vapour in natural gas in the gaseous phase is not considered undesirable, but condensation of water vapour causes difficulties. In city mains where natural gas has replaced manufactured gas, it has been necessary to saturate the gas with water vapour in order to keep the joints tight, otherwise the natural gas would dry out the regulator diaphragms and the joint packing. As too much water may cause trouble, a study of saturated conditions[17]

[10] *U.S. Bureau of Mines, Tech. Publ.*, 555.
[11] *Petr. World* (*L.A.*)., Nov., 1933, 40–44, Bibliography
[12] *U.S. Bureau of Mines, Tech. Publ.*, 539.
[13] *U.S. Bureau of Mines, Tech. Publ.*, 554.
[14] *Oil & Gas J.*, 5.10.33, **32** (20), 14, 30.
[15] *U.S. Bureau of Mines, R.I.*, 3216.
[16] *U.S. Bureau of Mines, R.I.* 3172.
[17] *Western Gas*, **8** (6), 15–17, 46–48.

and methods of saturation[18] is important. Water vapour may be needed in the natural gas in city mains, but in "bottled gas" any water vapour is a source of trouble. Water dissolved or entrained in the gas causes freezing of the regulators. This necessitates a dehydration of the gas by a special treatment, if water vapour is found to be present.[19]

Natural Gasoline.

It appears as though the natural gasoline industry were now on the upward trend. For two years there has been practically no building of natural gasoline plants, and now, at the end of 1933, there is more building in progress than there has been any time during that period. The average price of natural gasoline continued to decrease through 1932 and the first six months of 1933. The price increase during the last half of 1933 has been sufficient to encourage the construction of new plants.[20] Production figures[21] for :—

1931	1,831,918,000 gals.
1932	1,523,800,000 ,,

An innovation in natural gasoline plants is an unusually designed tank which permits the storage of natural gasoline under pressure. The bottom and top of the tank are of radial cone design and present a scalloped appearance. Another interesting feature of this tank is a specially constructed vent, the tank of which holds 100 gals. of glycerine. It is believed that this tank design will greatly reduce evaporation losses.[22]

With the design of natural gasoline plants, the pipe lines involved are an important factor. Charts have been devised to assist in solving this problem. The chart consists of a gas line flow diagram with parallel charts for the size of the pipe, temperature, pressure and length of the pipe. Examples are given showing calculations for determining pipe size under a given set of conditions.[23]

Army aviators have been warned about flying over certain of the areas where there are natural gasoline plants, as air tests have shown dangerous amounts of inflammable gases to be present, which might be ignited by the exhaust of the plane. Commercial lines flying over these areas have instructions to fly at high altitudes where there is no danger of igniting the gas.

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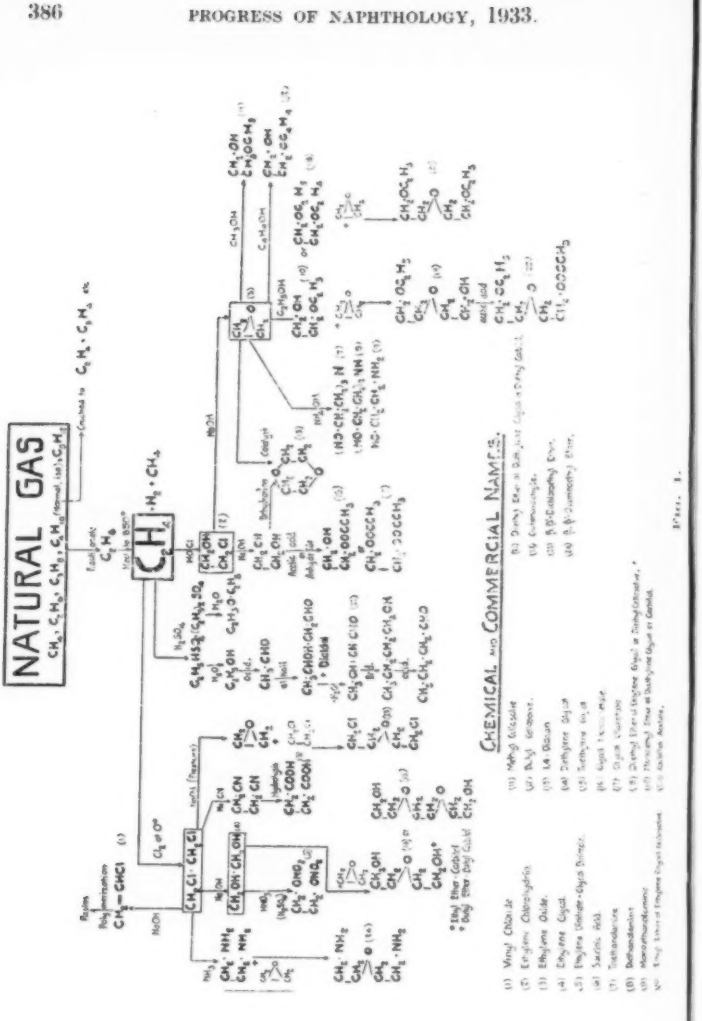
[18] *Gas Age Record*, **71**, 274–5.
[19] *Western Gas*, **8** (1), 55–6.
[20] *Oil & Gas J.*, 4.1.34, **32** (33), 25.
[21] Natural Gasoline—Statistical Appendix to Minerals Year Book, 1932–33 (B. of Mines).
[22] *Oil & Gas J.*, 9.11.33, **32** (25), 35.
[23] *Oil & Gas J.*, 30.3.33, **31** (45), 24.


NATURAL GAS
CHEMICAL AND COMMERCIAL NAMES.
(1) Vinyl Chloride
(2) Ethylene Chlorohydrin
(3) Ethylene Oxide
(4) Ethylene Glycol
(5) Diglycol Dihydrogen Phosphate
(6) Succinic Acid
(7) Tetrahydrofuran
(8) Butanediamine
(9) Monoethanolamine
(10) Methyl Cellosolve
(11) Butyl Cellosolve
(12) 1,4 Dioxan
(13) Diethylene Glycol
(14) Triethylene Glycol
(15) Tetraethylene Glycol
(16) Glycol Diacetate
(17) Glycol Dinitrate
(18) Diethyl Ether of Diethylene Glycol (or Diethylcarbitol)
(19) Monomethyl Ether of Diethylene Glycol (or Carbitol)
(20) Glycol Monoacetate
(21) Glycol Monoethyl Ether (or Cellosolve)
(22) Diethyl Ether of Diethylene Glycol (or Diethylcellosolve)
(23) Monomethyl Ether of Diethylene Glycol (or Carbitol Acetate)
(24) Diethyl Ether of Triethylene Glycol (or Triethylcellosolve)
(25) Monomethyl Ether of Triethylene Glycol (or Methylcarbitol)
(26) Diethyl Ether of Tetraethylene Glycol (or Tetraethylcellosolve)
(27) Monomethyl Ether of Tetraethylene Glycol (or Methylcarbitol Acetate)

Use as Fuel.

New uses of natural gas as an industrial fuel increase constantly. In the metal industry it is found suitable not only for foundries, but also for use in the metallurgical furnaces, one important

factor being the increase in efficiency and maximum flame temperature due to the reduction in excess air requirements as compared with other fuels.[24,25]

Another use for natural gas in the metallurgical industry is as a reducing agent for zinc ore. The earlier small scale experiments in this field have been continued with larger equipment at different temperatures and with different catalysts. There are indications that this process shows industrial possibilities.[26]

Butane and propane have found many new uses as fuels. One of the more recent is the use of butane as a fuel for rail motor cars. The Southern Pacific have been burning it in one of their specially constructed locomotives. The advantages claimed are: lower cost, increase in horse power, elimination of crank case dilution, elimination of smoke, smoother engine operation and probably a reduction in the cost of engine maintenance. The Union Pacific considered its use as fuel in their new 110 mile streamline train.[27,28]

The new Firekil torch designed for use in disinfecting poultry-houses, dairies, hog pens, etc., uses a liquified petroleum gas as fuel. By means of a special burner a maximum flame temperature of 2000° F. is produced. It is particularly adapted for use where chemical disinfectants are not efficient. The danger of fire when properly manipulated is held to be negligible.[29]

Chemical Uses.

The paper presented by Bowen and Nash at the World Petroleum Conference discusses the many chemical products derived from hydrocarbon gases.[30]

A chart, Fig. 1, prepared by Prof. A. Lowy shows the enormous possibilities of natural gas as a chemical reservoir.[31]

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[24] *Western Gas*, **9** (6), 10–11.
[25] *Iron Age*, **132**, Aug. 31, p. 11–13; Sept. 7, 14–17; Sept. 14, p. 20–2; Sept. 21, p. 13–15; Sept. 28, p. 36–7.
[26] American Institue of Mining and Metallurgical Engineers Contribution 9 (1933).
[27] *Oil & Gas J.*, 1.6.33, **32** (2), 33.
[28] *Western Gas*, **9** (12), 24.
[29] *Oil & Gas J.*, 14.9.33, **32** (17), 29.
[30] *Refiner*, 1933, **12**, 361, Bibliography.
[31] *Ind. Eng. Chem., News*, 1932, **10**, 6.

Crude Oil.

By W. H. Thomas, A.R.S.M. (Member).

A general review of literature, published in 1933, on Crude Oils reveals that comparatively little work has been carried out, although the subject provides ample opportunity for original research and investigation. Nevertheless, apart from the usual descriptions of various types of crude petroleums and their products, a little geochemical research has been reported, a considerable extension of which would be of immense value to the geologist and petroleum engineer as an aid to the complete study of oil-fields and also as a possible means for advancing the present state of knowledge regarding the origin of petroleum. It will also be seen in the following review that two attempts have been made to work out a system of classification for crude oils, and that further attention has been paid to naphthenic acids from petroleum.

No fresh study of American crudes has been published, but Nelson and Egloff, continuing their investigations, have been responsible for articles on Trinidad and Mexican petroleums. The first of these[1] describes the yields of products obtained from three typical crudes—paraffin, mixed base and naphthene—and gives details of the quality of motor spirit yielded by straight distillation and by cracking. In the second[2] the properties and distillation characteristics of Tuxpam, Panuco, Ochoa, Alamo Cerro Azul, Chapopote Nunez, Potrero del Llano, Tierra Blanca, Tateco Gonzalo, Topila and Zuneta crudes are given, together with the results of cracking tests on various products from Naranjos crude. The crudes are of two types, heavy asphaltic and light paraffin base.

With regard to European oilfields, the crude oils of Austria have been dealt with by Prof. Suida,[3] who has described the economic and technical importance of the Zistersdorfer oilfield in lower Austria. The oil from this field is of somewhat unusual type; it is a heavy asphalt-base oil practically free from wax and hard asphalt and contains no gasoline fractions. Full analyses of the crude oil and of the products obtained by laboratory distillation are given.

Keppeler,[4] in an article on the physical and chemical properties of North German petroleums, has tabulated data concerning the

[1] Nelson and Egloff. *Oil & Gas J.*, 2.2.33, **31** (37), 12. *J. Inst. Petr. Techn.*, 1933, **19**. Abs. No. 290.

[2] Nelson and Egloff. *Oil & Gas J.*, 9.3.33, **31** (42), 16. *J. Inst. Petr. Techn.*, 1933, **19**. Abs. No. 396.

[3] Suida. *Tag. Ber.*, 21.12.32. *J. Inst. Petr. Techn.*, 1933, **19**. Abs. No. 204.

[4] Keppeler. *Petr. Z.*, 20.9.33, **29** (37), 6 7. *J. Inst. Petr. Techn.*, 1933, **19**. Abs. No. 1084.

oils from the principal producing fields—Weitze Steinförde, Oberg-Olheim, Nienhagen, Thuringen and Volkenroda. He gives the depths of producing horizons, density, percentages of olefine, aromatic, paraffin and naphthene hydrocarbons and distillation ranges. In a continuation of their investigation of Ural petroleum, Zelinsky and Juriew[5] have examined the fraction boiling between 150–240° C. with regard to its content of aromatics, hydro-aromatics, paraffins and polymethylenes.

The products from Estonian shale oil have been described by Egloff and Nelson,[6] in particular those from the Kohtla and Eesti-Patendi retorts. The oil from the first of these contains little gasoline, the chief marketable products being diesel oil, lubricating oil and "Estobitumen." From the second is obtained an oil containing gasoline as well as light, medium and heavy oils. The authors also give details of cracking tests on the crude and topped shale oils.

Apart from those already mentioned, the only other crude oils which have formed the subject of publications are those of Japan. In a paper by Mizuta[7] a description has been given of the general properties and the composition of gasoline fractions of representative Japanese crude oils, particular attention being paid to the casing-head gasoline produced in the Kinsui oilfield of Tiwan. The type of compounds present is stated to be the same as in the gasoline from Shukoko crude. With regard to the latter, the same author[8] has studied the isolation of pure benzene by a freezing method. In a further publication,[9] dealing with the general constituents of Japanese petroleum, Kobayashi gives details of the fractions boiling above 200° C. at ordinary pressures. The material was fractionated under vacuum and the fractions refined with acid, neutralised and their constants determined. As a result of this work, the presence of certain definite constituents was proved by comparison of the data obtained with the known values for naphthene, polynaphthene and paraffin hydrocarbons.

Turning now to the geochemical researches already commented upon, Mitchell[10] has disclosed the fact that a mountain of asphalt

[5] Zelinsky and Juriew. *Brenn. Chem.*, 1934, **14**, 347–349. *J. Inst. Petr. Techn.*, 1933, **19**. Abs. No. 1086.

[6] Egloff and Nelson. *Oil and Gas J.*, 12.1.33, **31** (34) 14. *J. Inst. Petr. Techn.*, 1933, **19**. Abs. No. 300.

[7] Mizuta. *J. Soc. Chem. Ind. Japan*, 1933, **36** (6), 330B. *J. Inst. Petr. Techn.*, 1933, **19**. Abs. No. 1029.

[8] Mizuta. *J. Soc. Chem. Ind. Japan*, 1933, **36**, 448B. *J. Inst. Petr. Techn.*, 1933, **19**. Abs. No. 1134.

[9] Kobayashi. *J. Soc. Chem. Ind. Japan*, 1933, **36**, 553B. *J. Inst. Petr. Techn.*, 1934, **20**. Abs. No. 10.

[10] Mitchell. *Roads and Road Constr.*, 1.3.33, **11** (123), 75. *J. Inst. Petr. Techn.*, 1933, **19**. Abs. No. 301.

has been discovered at Sinai. The material appears to be a quartz sandstone impregnated with hard bitumen which has a penetration of 7 and no ductility. The bituminous sandstone, when mixed with a small proportion of asphaltic oil from adjacent wells, yields a paving material similar to Kentucky sandstone-asphalt. The occurrence, nature and origin of asphaltites in limestone and oil-shale deposits of Estonia have been dealt with by Kogerman.[11] From analyses of the materials, it is concluded that the bitumen found in Estonian limestone and oil shale is an asphaltite whose properties correspond closely to those of a grahamite. The author suggests that the "coals" of Vastergötland might also be asphaltites, and concludes that they have been formed *in situ* from organic sediments by biochemical changes in parallel with oil-shale formation. Toron[12] has commented on the interesting fact that the early wells in the Big Lake Pool, Texas, produced on completion a water-white oil, but after several months a dark coloured oil appeared. It was unfortunate that drilling difficulties prevented further production of the water-white oil, but the depth at which the change to heavy oil took place has been ascertained. Otin and Savenco,[13] by studying the effect of organic solvents on Matitza asphalt, have come to the conclusion that the material in question is a conversion product of petroleum and that in no case does petroleum originate from the asphalt.

In a publication dealing with the chemical composition of petroleum, Sachanen and Wirabianz[14] have studied its group composition without regard to individual compounds. From the results of analyses they have divided petroleums into six classes: (*a*) paraffin; (*b*) paraffin-naphthene; (*c*) naphthene; (*d*) paraffin-naphthene-aromatic; (*e*) naphthene-aromatic and (*f*) aromatic. Paraffin, naphthene and paraffin-naphthene oils are characterised by simple ring structure and long side chains. The paraffin-naphthene-aromatic type has more complex ring structures and shorter side-chains, while the naphthene-aromatic oils are highly polycyclic.

Severin[15] classifies Rumanian crude oils into two groups: (*a*) light paraffinic oils and (*b*) heavy paraffin-free oils. The latter are

[11] Kogerman. *J. Inst. Petr. Techn.*, 1933, **19**, 215. *J. Inst. Petr. Techn.*, 1933, **19**. Abs. No. 399.
[12] Toran. *Petr. Eng.*, 1933, **4** (7), 18. *J. Inst. Petr. Techn.*, 1933, **19**. Abs. No. 514.
[13] Otin and Savenco. *Petr. Zeit.*, 25.10.33 and 15.11.33, **29** (42), 1–5 and 13–77. *J. Inst. Petr. Techn.*, 1934, **20**. Abs. No. 68.
[14] Sachanen and Wirabianz. *Erdöl u. Teer*, 1933, **9**, 170. *J. Inst. Petr. Techn.*, 1933, **19**. Abs. No. 550.
[15] Severin. *Petr. Zeit.*, 15.7.33, **29** (28), 13. *J. Inst. Petr. Techn.*, 1933, **19**. Abs. No. 850.

divided into light, medium and heavy grades, but the former are generally more homogeneous. It is also of interest to note that the chemical composition of the oils varies with the geological age of the producing rock.

Tiutiunnikov and Pervuhin[16] have examined naphthenic acids from Baku crude, and concluded that fatty acids may be present in Baku oil in isomeric forms with melting points so low that the acids are liquid at ordinary temperatures; hence, the absence of higher fatty acids is not conclusively proved. In the same connection Pyhala[17] has studied the naphthenic acids present in Balakhany and Emba crude oils and in Rumanian fuel oil. He found that the acid content was 10–12 times greater after distillation, and suggests in explanation that this may be due to the masking of the naphthenic acids in the crude oil by complex substances which are decomposed during distillation. His final hypothesis is that these acids may be formed in petroleum as the result of oxidation reactions.

In conclusion, it should be pointed out that whereas the publications on crude oil during 1933 are only about 20 in number, there must be a very large amount of work still unpublished. If much of the unpublished work could be brought to light and correlated with the information already available, the advantages gained thereby, particularly from the geochemical standpoint, would far outweigh the problematical disadvantages due to political and commercial considerations.

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[16] Tiutiunnikov and Pervuhin. *Masloboino Zirovol Dilo*, 1933, (**3**), 8. *J. Inst. Petr. Techn.*, 1933, **19**. Abs. No. 1017.

[17] Pyhala. *Matt. Grasses*, 15.9.33 (305), 9942–44. *J. Inst. Petr. Techn.*, 1933, **19**. Abs. No. 1231.

Motor Spirits and Light Distillates.

By E. B. Evans, M.Sc., A.I.C. (Assoc. Member).

A very large volume of work continues to be published dealing with the properties and uses of motor fuels. The World Petroleum Congress, held in London in July, was the occasion for a considerable number of papers; some of these describe original work, while others give accounts of the present position of various branches of the subject.

One of the most noticeable features of 1933 has been the continued tendency (noted in the Report of last year) of many countries to compel by legislation the use of alcohol for blending with gasoline as a motor fuel. The movement is dictated largely by political and economic considerations and is mainly designed to benefit the agricultural interests; but whether it represents progress in either economics or technology is a much-debated question.

Similar factors are responsible for the energetic search now being prosecuted in many countries for other fuels which can be used in the internal-combustion engine in place of gasoline. The production of benzines for this purpose from shale and brown coal tars, and by the low-temperature carbonisation of coal, has been carried on for years, but recently coal-gas, coal-dust, hydrogen, polymerisation products from coke-oven gas and water-gas, and even producer-gas formed in a portable charcoal-generator, have been advocated for use as fuels for automobiles. Besides these, the use of gasoline is also menaced by the increasing use of Diesel engines for heavy road-vehicles.

The situation is made more difficult by the heavy taxation of gasoline, which has been found a fruitful source of revenue and in some countries used to subsidise the production of alcohol as a competitor. An interesting study of the effect of taxation on gasoline sales has been contributed by Swensrud.[1] A summary of the gasoline prices in the United Kingdom, together with the tax imposed, for the years 1922-1933, has appeared recently.[2]

Swensrud[3] has attempted to estimate the probable demand for gasoline in the next few years from a study of automobile registration figures. There are grounds for believing that a decline in the demand will occur. The world trade in gasoline is described by Mockler,[4] who also discusses the possible alterations in the trend of the markets.

(Figures in parentheses at end of reference refer to I.P.T. Abstract Numbers for 1933 unless otherwise stated.)

[1] *A.P.I. Proceedings*, May, 1933, Section II., p. 21.
[2] *Oil News*, 1933, **34**, 398.
[3] *Oil & Gas J.*, 16.3.33, **31** (43), 14. (489.)
[4] *Oil & Gas J.*, 3.11,32, **31** (24), 13. (196.)

The volatility and knock-rating of gasolines has been increased continually during recent years, and it is expected that the tendency will continue.[5] Research on the technical development and utilisation of motor fuels has been active, and an encouraging feature is the amount of technical co-operation which exists between the various groups of producing, marketing and consuming interests, with a view to furthering the economical use and rational testing of fuels. Committees for this purpose are active in America,[6] in Great Britain and on the Continent.

An interesting event has been the publication recently of new specifications for the supply of fuel for aircraft engines to the British Air Ministry. These specifications[7] admit, for the first time, the use of tetraethyl lead and of cracked gasolines, and call for octane numbers of 77 and 87 respectively.

The published work which has appeared since the last review on this subject is considered in more detail in the sections which follow.

Alcohol Fuels.

The production and use of alcohol-gasoline blends as motor fuels is now widespread in Europe, and, moreover, is encouraged in South America and, rather surprisingly, is receiving considerable support from some quarters in the U.S.A., the world's largest gasoline producer.

In France, the "poids lourds" grade must contain at least 25 per cent. and may contain up to 35 per cent. of alcohol, while the "tourisme" grade may have between 11 per cent. and 15 per cent.[8] The "poids lourd" must be coloured with rhodamine dye to prevent its use for adulteration of the "tourisme" spirit.[9,10] The use of these alcohol fuels does not seem to be altogether popular even in France. In Germany, importers of gasoline must take a certain proportion of the weight of their imports of alcohol from the Government Alcohol Monopoly. This proportion, which increased over a period of several years, has been 10 per cent. since October 1st, 1932. Gasoline as marketed may or may not contain alcohol; often a gasoline-benzole-alcohol blend in marketed.[11] Other European countries in which the use of alcohol mixtures is favoured by legislation include Sweden, Italy, Spain, Hungary and Czechoslovakia. It is stated that in the last-named

[5] Zeigenhain, *Oil & Gas J.*, 19.1.33, **31** (35), 20. (249.)
[6] Horning, *Oil & Gas J.*, 27.4.33, **31** (49), 15. (786.)
[7] Air Ministry Specifications D.T.D. 224, D.T.D. 230. H.M.S.O., 1933.
[8] *Ann. des Comb. Liquides*, 1933, **8**, 738.
[9] *Ann. des Comb. Liquides*, 1933, **8**, 1153.
[10] *Oil News*, 1933, **34**, 344.
[11] Fritzweiler & Dietrich, *Proc. World Petr. Congr.*, 1933, **2**, 784.

country the compulsory use of alcohol fuels has resulted in a decline in automobile sales.[12]

Interest in alcohol blends in the U.S.A. is centred round the production and utilisation of grain alcohol. It is considered that this outlet for surplus produce would help towards the higher grain prices desired.[13] The Illinois Farm Supply Company have, however, abandoned the sale of an alcohol-gasoline blend after several months' widespread marketing throughout the State of Illinois.[14] A discussion of the economics of production of fuel alcohol from agricultural products in the U.S.A. is given in the *Oil & Gas Journal*,[15] and also in a paper to the A.P.I. by G. G. Brown,[16] who also discusses the engine performance of such fuels. Various South American countries such as Argentine, Brazil, Chile and Panama have legislated for the use of alcohol blends, while a Bill is being introduced, although against considerable opposition, to make their use compulsory in Queensland. The Irish Free State is considering the erection of distilleries for the production of fuel alcohol from the surplus potato crop.[17,18,19,20,21] The situation in Japan is discussed by Hagiwara.[22] The main source of fuel alcohol in that country is molasses, and the product seems to be used without admixture with gasoline. Corbett[23] gives some useful information on alcohol for fuel purposes from the economic viewpoint.

The C.F.R. Committee have appointed a special sub-committee to investigate the alcohol fuel problem. A report[24] summarises the established facts in connection with blends containing 10 per cent. of alcohol. Fuel consumption is higher, starting more difficult, and tendency to vapour lock greater than with gasoline alone. The octane number is, however, raised by the addition. Ethyl alcohol is not so desirable for blending as some of the higher alcohols. Moreover, it is stated, alcohols can be produced more cheaply from petroleum than from agricultural products. Very

[12] *Petr. Times*, 1933, **30**, 658.
[13] *Oil News*, 1933, **34**, 389.
[14] *Petr. Times*, 1933, **30**, 626.
[15] *Oil & Gas J.*, 16.3.33, **31** (43), 10; 30.3.33, **31** (45), 16. (604.)
[16] *A.P.I. Proceedings*, May, 1933, Section II., p. 4 (see also *Oil, Paint & Drug Reporter*, 12.6.33, **123** (24), 43; 17.7.33, **124** (3), 38; 24.7.33, **124** (4), 28D; 31.7.33, **124** (5), 36. (1071.)
[17] *Petr. Times*, 1933, **30**, 656.
[18] *Oil News*, 1933, **34**, 424.
[19] *Oil News*, 1933, **34**, 390.
[20] *Oil News*, 1933, **34**, 428.
[21] *Petr. Times*, 1933, **30**, 466.
[22] *J. Fuel Soc.*, Japan, 1933, **12**, 46. (714.)
[23] *Petr. Times*, 1933, **30**, 459.
[24] Horning, *J.S.A.E.*, 1933, **33** (1), 29. (831.)

similar views have been expressed by a joint committee working under the auspices of the U.S. Bureau of Mines, and the American Automobile Association. A statement of conclusions has been issued in pamphlet form.[25] Arnstein[26] defends the use of alcohol blends on the grounds that alcohol serves to improve gasoline, not to replace it. Another discussion of the situation has been given in the *Automobile Engineer*.[27]

The stability of gasoline-alcohol-water mixtures has been examined by Christensen, Hixon and Fulmer,[28] and by Bridgeman and Querfeld.[29, 30, 31] The latter authors have determined the critical solution temperatures of a large number of blends; the source of the crude has little influence on the result, but cracked fuels and the more volatile gasolines have lower critical solution temperatures. The system ethyl alcohol-n-heptane has been studied by Ferguson, Freed and Morris.[32]

The above discussion deals exclusively with ethyl alcohol, but as a competitor for blending purposes, synthetic methanol has recently been given some attention. Methanol has the disadvantage of low calorific value and even when the materials are quite anhydrous it is only very slightly soluble in gasoline. To remedy this latter disadvantage, considerable work has been carried out to develop "blending-agents" which will permit of the production of methanol-gasoline blends of satisfactory water-tolerance. Suitable blending-agents include benzole and toluole, ethyl and the higher aliphatic alcohols and cyclohexane and methylcyclohexane. Various amines and phenols are also good blending agents, but other properties (*e.g.*, gumming tendency) make them unsuitable as components of motor fuel.[33] Howes[34] also considers the use of blending agents in a comprehensive paper dealing with the use of methanol as a motor fuel. Questions of miscibility, stability and engine performance of blends are fully discussed. Methanol alone has an application as a fuel for racing purposes. In Germany, it has recently been proposed to introduce as a fuel a mixture of methanol, ethanol and gasoline, and the performance of such blends in the engine has been examined by Schmidt.[35]

[25] Pamphlet published by *A.A.A.*, September, 1933, see also *Oil, Paint & Drug Reporter*, 1933, **123** (26), 37. (830.)
[26] *Petr. World*, 1933, **30**, 248. (1193.)
[27] *Auto. Eng.*, 1933, **23**, 238. (941.)
[28] Christenson, Hixon and Fulmer, *Iowa State Coll. J. Sci.*, 1933, **7**, 461.
[29] *Bur. Stand. J. Res.*, 1933, **10**, 841. (863.)
[30] *Bur. Stand. J. Res.*, 1933, **10**, 693.
[31] *Ind. Eng. Chem.*, 1933, **25**, 523.
[32] *J. Phys. Chem.*, 1933, **37**, 87. (241.)
[33] Gordon, *Proc. World Petr. Congr.*, 1933, **2**, 788.
[34] *J. Inst. Petr. Techn.*, 1933, **19**, 301. (601.)
[35] *Erdöl u. Teer*, 1933, **9**, 74. (281.)

Alternative Fuels.

Besides benzole, which is discussed in another of these reports, and alcohol-blend fuels, which are dealt with in the preceding section of this paper, a number of other sources of fuel have been proposed for the spark-ignition internal combustion engine. Little has been published on the use of acetone, ether, higher alcohols and similar materials, which find their main application in racing fuels, and these will not be discussed here. A number of liquid and gaseous products from sources other than petroleum have, however, been proposed as gasoline substitutes.

The use of coal-gas as a motor fuel has recently been revived, and is described in several papers by Walter.[36, 37, 38, 39] The gas is stored in steel bottles at 3000 lb. per sq. in., each bottle containing the equivalent of about a gallon and a half of gasoline. Road tests are stated to have given very satisfactory results.

The Erren hydrogen engine[40] runs on a mixture of hydrogen and oxygen from the electrolysis of water. Its use is suggested for submarine work on account of the innocuous character of the exhaust.

Somewhat less convenient, perhaps, are the portable charcoal- or producer-gas plants which have been used to some extent in this country and abroad.[41, 42, 43] The charcoal may be made separately or in the generator; the extra weight on the automobile carrying one of these units is about 2½ cwt. The chief advantage claimed for this system is economy, the fuel cost being about one-fourth that of gasoline. Staniland and Lee[44] discuss the use of pulverised coal in internal-combustion engines, but the ash content is at present an unsurmounted difficulty. The "Rupa" coal-dust motor[45] works on the Diesel principle.

The polymerisation of gases has also been employed to produce liquid fuels. Peters and Neumann[46] describe the polymerisation of coke-oven gas by means of the electric discharge and of an iron and nickel catalyst. The product of the electric discharge is acetylene and of the catalytic process, a mixture of unsaturated and aromatic hydrocarbons, 70 per cent. of which boils below

[36] *Trans. Inst. Min. Eng.*, 1933, **85**, 352. (1292.)
[37] *Int. Comb. Eng.*, 1933, **1**, 24.
[38] *Proc. World Petr. Congr.*, 1933, **2**, 764.
[39] *c.f.* also *Chem. Trade J.*, 4.11.32, **91**, 418. (97.) *Gas World*, 1932, **97**, Suppl. 13. (99.)
[40] *Mar. Eng.*, 1933, **56**, 15. (277.)
[41] *J. Fuel Soc.*, Japan, 1933, **12**, 68. (836.)
[42] Russel, *Proc. World Petr. Congr.*, 1933, **2**, 769.
[43] *Fuel Economist*, 1933, **9** (97), 56.
[44] *Auto. Eng.*, 1933, **23**, 358. (1293.)
[45] Pawlikowski, *Int. Comb. Eng.*, 1933, **1**, 6.
[46] *Brenn. Chem.*, 1933, **14**, 161. (797.)

150° C. Working on different lines Bowen and Nash[47] have produced liquids suitable for use as fuels and of excellent anti-knock value by the polymerisation of gaseous olefines, *e.g.*, of ethylene by aluminium chloride. These products appear to be iso-paraffinic in character, aromatics and olefines being almost completely absent.

Finally, there are the products obtained from coal by carbonisation or hydrogenation. This problem is discussed by Lander.[48] King[49] also discusses the production of motor spirits by the low-temperature process. "Hydrogenation-cracking" of the tars produced yields a further supply of motor fuel. It is stated that the Air Ministry are using low temperature spirit as aviation fuel. Some of the properties of this low temperature spirit are described by Manning.[50]

Little gasoline seems to have been produced so far by the hydrogenation of petroleum, but there is active interest in the hydrogenation of coal with this object in view. The process and the properties of the product were dealt with in several papers before the World Petroleum Congress in July.[51]

The cracking of brown-coal tars and shale-oils has also been found to give good yields of motor fuel of good quality, but high-temperature tars do not seem to be suitable for obtaining motor spirit in this way.[52]

The Composition of Gasoline.

In the course of the systematic investigation of the composition of an Oklahoma Mid-Continent petroleum, which is now being carried out by the United States Bureau of Standards, twenty-four hydrocarbons have now been isolated and their amounts estimated. During the year 1933 various workers, under the direction of E. W. Washburn, have published details of the separation of 1·1-dimethylcyclopentane and 2-methylhexane,[53] 2-methyl-heptane,[54] ethylbenzene,[55] and mesitylene, pseudo-cumene and hemimellitene.[56]

All the hydrocarbons so far isolated occur in the normal gasoline fraction, and vary in amount from 0·1 per cent. for ethylbenzene to 4·0 per cent. for n-octane and n-nonane, these amounts being

[47] *Proc. World Petr. Congr.*, 1933, **2**, 774.
[48] *Colliery Guard.*, 1933, **146**, 425. (602.)
[49] *Proc. World Petr. Congr.*, 1933, **2**, 757.
[50] *Proc. World Petr. Congr.*, 1933, **2**, 7.
[51] *e.g.*, Pier, *Proc. World Petr. Congr.*, 1933, **2**, 290; Ormandy and Burns, *Proc. World Petr. Congr.*, 1933, **2**, 295.
[52] Fisher and Morrell, *J.S.C.I.*, 1933, **52**, 228T. (940.)
[53] Bruun and Hicks-Bruun, *Bur. Stand. J. Res.*, 1933, **10**, 465. (548.)
[54] Leslie, *Bur. Stand. J. Res.*, 1933, **10**, 609. (779.)
[55] White and Rose, *Bur. Stand. J. Res.*, 1933, **10**, 639. (780.)
[56] Mair and Schicktanz, *Bur. Stand. J. Res.*, 1933, **11**, 665.

calculated on a 25 per cent. yield of gasoline from the crude. About 27 per cent. of the gasoline is now accounted for on this basis.

Sachanen and Wirabianz,[57] in the course of a general investigation of the composition of petroleum, give some information on the gasoline fraction. They conclude that the fraction up to 150° C. contains benzene, toluene and the xylenes, while from 150 to 200° C. occur cumene, butyl- and amylbenzene and propyltoluene.

Little work appears to have been done recently on the sulphur compounds of gasoline, with the exception of that described in a paper by Shipley.[58] Turner Valley naphtha was found to have a sulphur content of from 0·15 to 0·19 per cent. consisting of sulphides, disulphides and mercaptans; thiophenes were present in very small amount. Morrell and Egloff[59] find that the sulphur content of an untreated Californian cracked distillate increases with fractions of increasing boiling-range up to about 400° F. when a falling-off occurs.

Mizuta[60] gives the group composition of a casinghead gasoline from the Kinsui field.

Detonation and Anti-knocks.

Much work has been carried out during the past year on various aspects of the complex problem of detonation. The theory of the mechanism of this phenomenon is still by no means clear, in spite of many excellent investigations. The fundamental oxidation reactions which occur, both in tubes and in the engine cylinder, have been studied by several investigators.[61, 62] Campbell, Whitworth and Woodhead[63] examined the rates of detonation in carbon monoxide-oxygen mixtures, and found that there was an almost linear increase of speed with increase in the proportion of combustible gas over most of the detonation range. The speed seems to depend on the calorific value and density of the gas mixture. Maas and Ewing[64] showed that the presence of nitrogen was essential to the phenomenon of " critical " ignition of hydrogen-oxygen mixtures. Evidence in support of the oxidation of paraffin hydrocarbons by hydroxylation, the formation of formaldehyde and subsequent oxidation of this to carbon dioxide has been obtained by Akita.[65] The number of critical inflexion points

[57] *Erdöl u. Teer*, 1933, **9**, 170. (550.)
[58] *Canad. J. Res.*, 1933, **8**, 119. (395.)
[59] *Proc. World Petr. Congr.*, 1933, **2**, 10.
[60] *J. Soc. Chem. Ind.*, Japan, 1933, **36** (6), 330B (1029).
[61] Francis, *J.S.C.I.*, 1933, **52**, 926. (52 of 1934.)
[62] Bone, *J.S.C.I.*, 1933, **52**. 905. (53 of 1934.) *J.C.S.*, 1933, 1599.
[63] *J.C.S.*, 1933, **134**, 59. (233).
[64] *J. Phys Chem.*, 1933, **37**, 13. (234.)
[65] *J. Soc. Chem. Ind.*, Japan, 1933, **36**, 436B. (1005.)

(sudden pressure rises) obtained by slow heating of the mixture of paraffin vapour and air is equal to the number of carbon atoms in the molecule, indicating that the combustion proceeds step by step. Steele[66] discusses the primary dehydrogenation theory and its consequences, while maximum flame temperatures for various gases have been measured by Lurie and Sherman.[67]

The combustion of fuels in the engine itself has been investigated by several workers. Egerton and Smith[68] find that the amount of peroxide formed in the combustion is connected with the cracking of the fuel. The spectrographic method of investigation has been applied by Withrow and Rassweiler.[69,70] They find, from spectrographic photographs of the gases, taken while the engine is running, that chemical changes occur in the fuel mixture prior to ignition, these effects being more pronounced when knocking combustion is obtained. They showed, further, that formaldehyde is one of the products formed in the non-inflamed gases prior to knocking; this compound was not observed when the fuel mixture was far removed from any tendency to knock. These observations are interesting to compare with those of Akita[65] on the oxidation of paraffin-air mixtures. Steele[71] has examined the change in the infra-red radiation from an engine, using various window positions and mixture strengths. In another paper[72] this author states that no evidence of peroxide could be found by him in the engine cylinder, and considers that these experiments do not support the Callendar peroxide theory of knocking. A discussion of the relation between ignition temperatures and detonation values of fuels is given by Schäfer,[73] who considers that ignition indices, determined by Jentsch's method, may form a suitable basis for a standard method of test.

The obscure nature of the reactions occurring when mixtures of hydrocarbon vapours and air are burned leaves us still without any comprehensive theory of the relation between the chemical constitution of fuels and their knocking value. During the past year, however, a considerable amount of work has appeared on the knock-values of individual pure hydrocarbons. Lovell, Campbell and Boyd[74] have now published data on the detonation

[66] *Nature*, 1933, **131**, 724. (716.)
[67] *Ind. Eng. Chem.*, 1933, **25**, 404. (428.)
[68] *Nature*, 1933, **131**, 724. (717.)
[69] *Ind. Eng. Chem.*, 1933, **25**, 923. (1066.)
[70] *Ind. Eng. Chem.*, 1933, **25**, 1359. (51 of 1934.)
[71] *Ind. Eng. Chem.*, 1933, **25**, 388. (430.)
[72] *Ind. Eng. Chem. Anal.*, 1933, **5**, 202. (710.)
[73] *Proc. World Petr. Congr.*, 1933, **2**, 218.
[74] *Ind. Eng. Chem.*, 1933, **25**, 1107. (1127.)

characteristics of the naphthene hydrocarbons, on the lines of their very comprehensive work on the paraffin and olefine hydrocarbons. In the most recent paper, they describe the detonating properties of 69 naphthene hydrocarbons, including five-, six- and seven-membered ring compounds, both saturated and unsaturated. The results are expressed in terms of "aniline equivalent" and the effects of structure are fully discussed. A comparison is given between these results, and some other work, and it is concluded that these ratings have a real value, since a similar order is obtained on different engines and by different workers. A correlation of most of the work on this phase of the subject has been given by Garner, Evans, Sprake and Broom,[75] who have converted the results in the literature to "blending octane numbers." They find, in general, excellent agreement, considering the diverse test-engines and methods employed. The same authors have considered the effect of the concentration of a hydrocarbon in a base fuel on the octane number of the blend, and the relation between the blending value and the knock value of the pure hydrocarbon alone.

A report on the work of the Cracked Fuels Committee of the Institution of Automobile Engineers[76] describes work carried out on olefines, including the gaseous members of the series, on the E.5, E.35 and S.30 engines. Ethylene has a tendency to pre-ignite when used alone, especially in the larger bore engines. The first data of this kind on an acetylene hydrocarbon has recently been published by Bowen, Nash and Garner[77] who have examined heptine-1 in this way. Similar work on hydrocarbons has been carried out by Schmidt and his collaborators[78,79] who include several aliphatic alcohols in their work, and make the interesting observation that the polymerisation products of cyclopentadiene and styrene have higher anti-knock values than the original hydrocarbons.

The general relations between the composition of a gasoline and its octane number are discussed by Trusty.[80] Ward and White[81] have attempted to relate anti-knock values of gasolines with volatility and the amount extracted by liquid sulphur dioxide, but they did not obtain very consistent results. Sulphuric acid refining leads to a loss of octane number of gasolines and this loss has been analysed into loss through evaporation of light fractions and loss

[75] *Proc. World Petr. Congr.*, 1933, **2**, 170.
[76] Garner, *J.I.A.E.*, December, 1932, p. 40. (50.)
[77] *Nature*, 1933, **131**, 410. (1126.)
[78] Hofmann, Berlin and Schmidt, *Brenn.-Chem.*, 1933, **14**, 326. (1125.)
[79] Schmidt, *Proc. World Petr. Congr.*, 1933, **2**, 181.
[80] *Nat. Petr. News*, 21.12.32, **24** (51), 29. (232.)
[81] *Oil & Gas J.*, 1.6.33, **32** (2), 38. (872.)

through acid solution and polymerisation.[82] Similar investigations have been carried out by Born,[83] who concludes that little loss of octane number need occur with proper conditions of acid treatment of almost any pressure distillate.

Trimble[84] has examined the knock-ratings and lead susceptibilities of natural and vapour-recovery gasolines. The former have a greater lead response. A rather complicated series of equations for expressing the lead susceptibility of gasolines has been developed by Hebl, Rendel and Garton.[85] From this mathematical treatment a chart is constructed from which the lead susceptibility can be obtained from the octane number of the gasoline and the octane number of the fuel with one concentration of lead tetraethyl.

Three papers [86,87,88] discuss the mechanism of the thermal decomposition of lead tetraethyl and lead tetraphenyl. Some very interesting observations have been made by D. B. Brooks[89] on the effect of ozone as a knock-inducer. The effect is of the same magnitude as, but opposite to, that of lead tetraethyl, and varies in degree according to the fuel to which the ozone is added.

The effect of jacket temperature on the octane number of fuels has been investigated by Peletier.[90] The fall in rating with increased jacket temperature appears to depend both on the rating at 100° C. and on the chemical composition of the fuel; cracked spirits show a greater sensitivity to temperature than do straight-run gasolines. An interesting review of recent work in Germany on the combustion and knocking of fuels has also been published.[91]

Gum Formation in Gasoline.

One of the most interesting publications on the subject of gumming which has appeared during the year, is the paper by Flood, Hladky and Edgar[92] which has been so widely quoted in the form in which it appeared as an American Chemical Society Preprint in 1930. In the work described, a number of pure olefines were dissolved in straight-run gasoline and bomb oxidation and storage tests carried out on the blends. It was found that the greatest amount of gum was formed from aliphatic or cyclic

[82] Wirth, Kanhofer and Murphy, *Oil & Gas J.*, 31.7.33, **32** (8), 13. (1040.)
[83] *Nat. Petr. News*, 5.4.33, **25** (14), 23. (568.)
[84] *Oil & Gas J.*, 19.1.33, **31** (35), 16. (247.) *Ibid.*, 18.5.33, **31** (52), 58. 873.)
[85] *Ind. Eng. Chem.*, 1933, **25**, 187. (235.)
[86] Meinert, *J.A.C.S.*, 1933, **55**, 979. (343.)
[87] Dull and Simons, *J.A.C.S.*, 1933, **55**, 4328. (1139.)
[88] Leermakers, *J.A.C.S.*, 1933, **55**, 4508. (69 of 1934.)
[89] *J. Inst. Petr. Techn.*, 1933, **19**, 835. (1226.)
[90] *Proc. World Petr. Congr.*, 1933, **2**, 165.
[91] Philippovich, *Proc. World Petr. Congr.*, 1933, **2**, 210.
[92] *Ind. Eng. Chem.*, 1933, **25**, 1234. (1245.)

diolefines or from aromatics with an olefinic linkage in the side-chain ; the gumming process is almost invariably associated with oxidation. Martin, Gruse and Lowy[93] have found that gum formation varies very much between different fractions of a vapour-phase cracked gasoline. For example, between 63 and 146° C., the fractions 74–79°, 102–107°, and 124–129° C. show the largest amounts of gum. These authors also consider that gum-formation is mainly due to such compounds as conjugated diolefines, cyclic olefines, etc., but they do not think that a gasoline can be satisfactorily stabilised by treatments which remove only a small proportion of the unstable compounds. Gum formation is accelerated by the presence of mercaptans, which form high-boiling resinous compounds with dienes (*e.g.*, ethyl mercaptan and cyclopentadiene).[94] The formation of colour in gasoline is a very complicated phenomenon, but the yellow colouration is probably due to the polymerisation of unsaturated hydrocarbons.[95] The action of ultra-violet light on cracked gasoline has received some attention, chiefly with a view to using the phenomenon as the basis of a test method.[96,97] Whereas Vellinger and Radulesco find that oxygen is essential for the formation of gum, Freund holds the opposite view ; he finds also that gums produced under different conditions (ultra-violet light exposure, oxygen-gum test, etc.), differ chiefly in their oxygen content.

Kogerman[98] has studied the thermal effects of the reaction between a benzene solution of stannic chloride and unsaturated hydrocarbons. Stephens[99] discusses the theory of autoxidation with reference to peroxides and other addition compounds.

The relationship of the results of storage to the various test-methods for gum-stability is still far from being elucidated. A recent paper[100] which discusses the significance of most of the test-methods that have so far been proposed, indicates that none of these is wholly satisfactory in predicting gum-formation in practice ; even the amount of formed gum which the engine will tolerate has not been established. Many refiners still believe that the copper dish method gives a reliable indication of the stability of gasolines.[101] Winning and Thomas[102] suggest the use of the bomb method in

[93] *Ind. Eng. Chem.*, 1933, **25**, 381. (439.)
[94] Kruber and Schade, *Brenn. Chem.*, 1933, **14**, 124. (832.)
[95] Trusty, *Refiner*, 1933, **12**, 53. (347.)
[96] Vellinger and Radulesco, *Ann. des Comb. Liq.*, 1933, **8**, 883. (1243.) *Proc. World Petr. Congr.*, 1933, **2**, 103.
[97] Freund, *Proc. World Petr.*, 1933, **2**, 108 ; *Brenn. Chem.*, 1933, **14**, 61.
[98] *Proc. World Petr. Congr.*, 1933, **2**, 113.
[99] *J. Phys. Chem.*, 1933, **37**, 209. (358.)
[100] Egloff, Morrell, Wirth and Murphy, *Proc. World. Petr. Congr.*, 1933, **2**, 85.
[101] Murphy and Wirth, *Oil & Gas J.*, 23.3.33, **31** (44), 24. (552.)
[102] *Ind. Eng. Chem.*, 1933, **25**, 511. (551.)

conjunction with the copper dish, in arriving at a prediction of stability. According to Rogers, Bussies and Ward[103] an induction period of 400 min. in the Voorhees test corresponds to about six months storage at 35° C. in a bottle, or to a year of storage in vented iron barrels at atmospheric pressure. W. H. Thomas[104] considers that it would be better, in view of the difficulty of correlation,to refine gasoline to the same time-gum stability curve as a selected product which experience has shown to be entirely satisfactory in use. That incubation in air at 35° C. for 20 hr. should not increase gum content by more than 10 mgms. per 100 mls. is considered a satisfactory test by Mardles and Moss[105]; this test has been adopted by the British Air Ministry in their new Specifications DTD. 224 and DTD. 230 for aviation fuel.

The rate of gum formation in gasolines and benzoles is now controlled very largely by the addition of anti-oxidants or "inhibitors," which usually consist of phenolic or amino derivatives of aromatic hydrocarbons. A large number of papers deal with the evaluation and application of these materials and discuss the relations of their structure and efficacy.[106–111] It seems generally to be agreed that a satisfactory inhibitor should be cheap, effective in inhibiting colour and gum formation and loss of octane number, even when used in very small quantities; should not itself impart colour to the gasoline; should be readily soluble in gasoline and but slightly so in water; and be sufficiently volatile to vaporise with the gasoline. With reference to the addition of colour by the inhibitor it is of interest to note a patent[112] which covers the use of an inhibitor which is also a dye. An attempt has been made by Scheumann[113] to evaluate inhibitors by means of a "gum inhibitor index" which is the quotient of the reduction of potential gum by the concentration of the inhibitor. A "colour-stability index" was similarly derived.

The Volatility of Motor Fuels.

Considerable interest continues to be shown in the study of the volatility of motor fuels as it affects the performance of gasoline

[103] *Ind. Eng. Chem.*, 1933, **25**, 397. (438.)
[104] *Proc. World Petr. Congr.*, 1933, **2**, 122.
[105] *Proc. World Petr. Congr.*, 1933, **2**, 116.
[106] Egloff, Morrell, Lowry and Dryer, *Ind. Eng. Chem.*, 1932, **24**, 1375. (55.). *Oil & Gas J.*, 30.3.33, **31** (45), 64. (679.) *Proc. World Petr. Congr.*, 1933, **2**, 50.
[107] Rogers and Voorhees, *Ind. Eng. Chem.*, 1933, **25**, 520. (570.) *Proc. World Petr. Cong.*, 1933, **2**, 63.
[108] Hoffert and Claxton, *J.S.C.I.*, 1933, **52**, 25. (265.) *Proc. World Petr. Congr.* 1933, **2**, 69.
[109] Mardles, *Proc. World Petr. Congr.*, 1933, **2**, 57.
[110] Thomas, *Proc. World Petr. Congr.*, 1933, **2**, 44.
[111] Conine, *Oil & Gas J.*, 24.11.32, **31** (27), 14. (259.)
[112] Stand. Oil Dev. Co. E.P. 383,511, 17.11.32. (90.)
[113] *Nat. Petr. News*, 15.4.33, **25** (14), 29. (553.)

engines. The A.S.T.M. distillation curve can give much information in this respect, it being possible to predict starting, vapour lock, acceleration and dilution effects from it.[114] McCoull[115] has examined the effect of volatility and engine conditions on fuel economy. Oberfell and Alden[116] propose to define the "volatility index" of a fuel as the difference between 284° F. (which is the maximum permissible 50 per cent. point for U.S. motor gasoline) and the 50 per cent. evaporated point for the gasoline: they consider that the effective volatility is well represented by the 50 per cent. point. Similar views are held by Brown,[117] (*cf.* also[118]) who finds also that roughly the same loss in performance (about 2 per cent.) results from a drop of 12 octane units below the requirement of the engine or from a drop of 10 in the volatility index.

The starting properties of fuels have been discussed by Brown,[119] by Whatmough,[120] and by Hoffert and Claxton.[121] Brown has determined the properties of a fuel which must be vaporised to give various starting properties, *e.g.*, with less than 5 per cent. starting is practically impossible, while easy starting requires at least 25 per cent. to be vaporised. The lowest temperature for easy starting is about 130° F. below the 10 per cent. A.S.T.M. temperature. Hoffert and Claxton have worked out a method for evaluating starting properties by the number of engine revolutions required for firing; among their interesting results is that the starting properties of certain benzole-gasoline blends are better than those of either constituent alone. This method of evaluation has been used by Whatmough, who considers that 20 revolutions to fire represents the useful starting limit; a mixture strength of at least 3:1 is required under winter conditions.

The vapour-locking tendencies of cars have been investigated by the C.F.R. Committee and the Natural Gasoline Association of America, and a formula connecting Reid vapour-pressure and vapour-locking temperature has been deduced from the results on about 50 cars.[122, 123]

Some interesting experiments on the relation between fuel, volatility and carburettor freezing (separation of ice-crystals) have been described by Clothier.[124] From tests with a laboratory apparatus, determining the spray temperatures obtained with

[114] Blair and Alden, *Ind. Eng. Chem.*, 1933, **25**, 559. (540.)
[115] *J.S.A.E.*, 1933, **33**, 363. (44 of 1934.)
[116] *Oil & Gas J.*, 19.1.33, **31** (35), 14. (248.)
[117] *Oil & Gas J.*, 18.5.33, **31** (52), 51. (938.)
[118] Anon., *Nat. Petr. News*, 25.5.33, **25** (21), 17. (784.)
[119] *Oil & Gas J.*, 19.1.33, **31** (35), 13. (278.)
[120] *Auto. Eng.*, 1933, **23**, 371. (1247.)
[121] *Engineering*, 1933, **155**, 300. (490.)
[122] White and Gary, *Oil & Gas J.*, 17.11.32, **31** (26), 62. (186.)
[123] Bridgeman, White and Gary, *J.S.A.E.*, 1933, **32**, 157. (484.)
[124] *Aero. Res. Comm.*, Report, 9, and Memos., 1933, No. 1549.

various fuels under different conditions, it was concluded that the lowering of temperature due to evaporation is dependent on the temperature and pressure of the intake air, the humidity of the air and on the volatility of the fuel. The 25 per cent. distilled points seems to give the best indication of the relative tendency of fuels to cause freezing.

A critical review of the methods available for computing the vaporisation characteristics of petroleum fractions is given by Brown and Katz.[125] Several papers have been published dealing with the vapour-pressures of hydrocarbons, which are of interest in connection with such work as is discussed above.[126–130]

Miscellaneous Work.

The dyeing of gasoline and the oil-soluble dyes used for this purpose are discussed by Clarkson.[131]

Gasoline presents numerous problems in storage and handling, as regards loss by evaporation and fire-risk. Larson[132] and May[133] deal with special types of storage tanks and safety devices; the risk of ignition by static charges is increased by excessive rates of flow of gasoline in pipe-lines.[134]

Another problem concerns the advisability of adding small amounts of lubricating oil to gasoline.[135,136] Opinion seems to be that the addition is warranted during the running-in period; fuel consumption may be slightly improved, but carbon formation is stated to be somewhat increased.

A convenient chart for blending gasolines to a desired A.P.I. gravity has been designed by Steele.[137] Carbon formation in the engine may be partly due to the gasoline, according to Stroud.[138] The presence of high-boiling or gum-forming constituents are the responsible factors.

A considerable amount of gasoline is used in the U.S.A. for heating purposes, in pressure appliances, and it is essential for this purpose that the fuel should be of the correct volatility, free from gumming and corrosive properties.[139]

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[125] *Ind. Eng. Chem.*, 1933, **25**, 1373. (42 of 1934.)
[126] Deitz, *J.A.C.S.*, 1933, **55**, 472. (226.)
[127] Tongberg and Johnston, *Ind. Eng. Chem.*, 1933, **25**, 733. (860.)
[128] Cummings, Stone and Volante, *Ind. Eng. Chem.*, 1933, **25**, 728. (862.)
[129] Bromiley and Quiggle, *Ind. Eng. Chem.*, 1933, **25**, 1136. (1119.)
[130] Francis and Robbins, *J.A.C.S.*, 1933, **55**, 4339. (43 of 1934.)
[131] *Oil & Gas J.*, 30.3.33, **31** (45), 50. (571.)
[132] *Proc. World Petr. Congr.*, 1933, **1**, 544.
[133] *Proc. World Petr. Congr.*, 1933, **1**, 551.
[134] Müller, *Erdöl u. Teer*, 1933, **9**, 222. (536.)
[135] Conine, *Oil & Gas J.*, 29.12.32, **31** (32), 9. (284.)
[136] Foster, *Nat. Petr. News*, 1.3.33, **25** (9), 26. (423.)
[137] *Petr. Eng.*, 1933, **5** (3), 56.
[138] *Oil & Gas J.*, 6.4.33, **31** (46), 12. (708.)
[139] St. John and Grubb, *Oil & Gas J.*, 29.6.33, **32** (6), 16. (1063.)

Gasoline Engines and Knock-Testing.

By C. H. Barton, M.A., A.I.C. (Member).

Engines.

For the year ending November, 1933, there has been an increase of slightly over 20 per cent. in the number of new private cars registered in Great Britain in comparison with those of the twelve months ending November, 1932. The increase in registrations is principally in the cars of 10 h.p. and lower, Treasury rating. This class accounts for 59 per cent. of the new registrations in 1933, against 50 per cent. in 1932. There has actually been a decrease in the proportion of new cars in the 11–20 h.p. class during 1933, the percentage being 36 in comparison with 46 per cent. during 1932. In the categories of 21 h.p. and over the new registrations for 1933 are 4·2 per cent. for 1933 and 3·7 per cent. for 1932.

The tendency to revert to 4-cylinder at the expense of 6-cylinder engines, especially in the smaller types, below 1½ litre capacity, continues. This development has been favoured by the increasing adoption of flexible engine mountings and balanced crankshafts, both of which produce greater smoothness of running.

One English maker is now fitting hardened steel cylinder liners. Light (aluminium) alloy pistons are practically universal, but in one or two cases composite pistons with aluminium head and cast iron skirt are employed.

Compression ratios as a whole are higher in 1933 than in 1932. There are now a number of engines in some cases, it is true, of the sports type, with compression ratios between 6 and 7 : 1.

Owing to the increase in size and speed of crankshaft journals, there is a tendency for oil temperatures to rise. In consequence, pressed steel oil sumps have been replaced in some instances by light alloy sumps of better conductivity.

Circulation of water for engine cooling by means of a centrifugal pump or water impeller has largely displaced the thermo-syphon system, which is now mainly used only in small engines. Most medium and high priced cars have thermostatic control of the temperature of the water in the cylinder jacket, either by means of radiator shutters or a valve in the water outlet pipe from the cylinder block.

Four speed gear boxes are in general use in English cars, usually with two or more constant mesh silent gears. Devices for assisting easy gear changing—*e.g.* synchromesh, free-wheel or pre-selector gear box are also incorporated in the majority of makes.

In aircraft engines development has been in the direction of increasing specific power output by supercharging and raising compression ratios, both of which have resulted in a demand for

higher anti-knock values in aviation gasolines. The increasing anti-knock requirements and the issue of an Air Ministry specification allowing the use of lead tetraethyl in high octane number aviation gasoline (DTD. 230, dated August 1933), have directed attention to the study of the effect of ethyl fluid on valves. This question has, of course, already received much attention in the U.S.A., and internally cooled exhaust valves are in common use in high-duty air-cooled engines. Covering of valves and valve seats with special alloys such as stellite (cobalt, chromium and tungsten), which are highly resistant to wear and corrosion, is also employed in America.

Knock-Testing.

The period under review has seen a considerable extension in the use of the C.F.R. engine and the adoption by the A.S.T.M. on March 7th, 1933, of the C.F.R. Motor Method[1] as a tentative standard for knock-rating under the designation D. 357–33T.

The C.F.R. Motor Method has incurred some adverse criticism both in America and Europe. In America the objection has been raised that the Motor Method unduly derates cracked gasolines[2] in comparison with straightrun fuels, the octane numbers being 5 or 10 lower than those given by the C.F.R. Research Method, while straightrun gasolines generally show octane numbers less than 5 units lower by Motor than by Research Method. Other objections[3] to the Motor Method have been based on the opinion that the cars used in the Uniontown tests and the conditions of the tests were not representative of motoring in general. Hubner and Murphy[4] consider that the Uniontown results on which the Motor Method is based show the impracticability of working out a method of knock-testing in a single cylinder engine which will agree with the diverse ratings obtained with different cars on the road. The car results, however, indicate that a reduction in tendency to detonate might be effected by an improvement in design—*e.g.*, in regard to shape of the combustion space, cooling efficiency and volumetric efficiency.

The C.F.R. engine and the Motor Method of test were discussed at the knock-rating section of the World Petroleum Congress[5] held in London in July, 1933. Amongst other criticisms of the Motor Method, exception was taken to the high temperature,

[1] Veal, Best, Campbell and Holaday, *J.S.A.E.*, March, 1933, 105; Discussion, Ibid., May, 1933, 187; A.P.I. 13th Annual Meeting, 1932, Sect. III., 139; Boyd and Veal, *Proc. World Petr. Congr.*, 1933, **2**, 139.
[2] R. C. Conine, *Oil & Gas J.*, 2.2.33, **31** (37), 26.
[3] *World Petroleum*, Oct., 1933, 338.
[4] *Proc. World Petr. Congr.*, 1933, **2**, 154; *Oil & Gas J.*, 21.9.33, **32** (18), 15.
[5] *Proc. World Petr. Congr.*, 1933.

namely 300° F., to which the air-fuel mixture is heated before it reaches the inlet port. The objections to the high mixture temperature were: (*a*) that it was higher than the temperatures reached in the inlet manifolds of automobile engines; (*b*) that it would promote chemical reaction between the fuel and air before the mixture reached the cylinder; and (*c*) that it was higher than the mixture temperature, namely, 260° F. recently found[6] to be suitable for rating gasolines for supercharged air-cooled aviation engines of British manufacture, although the latter apparently work at considerably higher cylinder temperatures than automobile engines. Resolutions were passed by the knock-rating section of the Congress to the effect that the problem of knock-rating required renewed study on an international basis in order to develop a method of test in the C.F.R. engine for general acceptance for determining the anti-knock value of motor gasolines. The work under contemplation included the testing of gasolines in automobiles under service conditions, and the necessity for dealing with alcohol-gasoline and benzol-gasoline mixtures amongst the fuels examined was emphasised.

A paper by Becker and Kass[7] presented at the World Petroleum Congress discusses the question of sub-standard gasolines for knock-testing with particular reference to the fuels A_2, C_4, etc., prepared and sold by the Standard Oil Development Company. In order to lessen the number of variables in knock-testing it is recommended by the authors that laboratories should preferably employ the same sub-standard fuels.

The effect of cylinder jacket temperature on knock-rating in single-cylinder testing engines—namely, the C.F.R., Ricardo E. 35, Series 30, and Armstrong engines—has been investigated by Peletier,[8] who shows that the absolute anti-knock value of iso-octane-heptane mixtures falls in all the engines as the jacket temperature is raised. On the average, gasolines are more affected by temperature than octane-heptane blends, and consequently the author suggests that more suitable standards than octane-heptane should be looked for.

Work on the knock-rating of pure hydrocarbons has been continued during 1933. Garner, Evans, Sprake and Broom[9] have examined certain hydrocarbons on the Series 30 engine at 212° and 300° F. cylinder jacket temperatures, and for a number of pure hydrocarbons have correlated published results in terms of a

[6] D. R. Pye, The Knock Rating of Aviation Fuels, *Proc. World Petr. Congr.*, 1933, **2**, 186.
[7] *Proc. World Petr. Congr.*, 1933, **2**, 150.
[8] *Proc. World Petr. Congr.*, 1933, **2**, 165.
[9] *Proc. World Petr. Congr.*, 1933, **2**, 170

common system of measurement. In this work mixtures containing 20–30 per cent., by volume, of pure substances in a standard gasoline were tested for knock-rating, and the effective or "blending" octane number of the pure hydrocarbon calculated, assuming a linear relationship between octane number and volume composition of the mixture. The results are compared with those of other investigators and are found to be in general agreement, particularly with the work of Lovell, Campbell and Boyd.[10] The latter have continued their work on pure hydrocarbons, and have published a paper[11] on the knocking characteristics of a large number of naphthene hydrocarbons in which it is shown that the relations between chemical structure and knocking tendency are similar to those of paraffin and olefine hydrocarbons. The knock-ratings of certain unsaturated hydrocarbons are discussed by Garner[12] in a report of the Empire Motor Fuels Committee.

Brooks[13] has recorded the strong pro-knock effect of oxone, 0·002 per cent. in the ingoing air/fuel mixture producing a detectable increase in detonation in the C.F.R. engine. Egerton and Smith[14] show, by taking samples of gases at various periods from the combustion space, the presence of peroxides and aldehydes during detonation. They also find that metallic anti-knock materials (lead and thallium) are only effective when oxidised before entering the cylinder. Steele,[15] by taking gas samples from the combustion space of an engine, has detected the presence of an oxidising agent which increases in concentration during the exhaust stroke, reaches a maximum early in the inlet stroke and then decreases in concentration. No evidence for the presence of peroxides was found in the gases either under knocking or non-knocking conditions. Steele[16] suggests that knock is due to the formation from the fuel of free hydrogen which causes detonation by reason of its high rate of reaction with the oxygen present.

In the matter of methods and instrumentation of knock detection, Paul and Albert[17] show that sound intensities increase when detonation occurs. Piezometric effects of knocking are described by Serruys.[18] Spectrographic observations during combustion have been taken by Rassweiler and Withrow,[19] using an engine provided

[10] *Ind. Eng. Chem.*, 1931, **23**, 26, 555.
[11] *Ind. Eng. Chem.*, 1933, **25**, 1107.
[12] *Proc. Inst. Aut. Eng.*, 1933, XXVII., 586.
[13] *J. Inst. Petr. Techn.*, 1933, **19**, 835.
[14] *Nature*, May 20, 1933, 725.
[15] *Ind. Eng. Chem., Anal.*, 1933, **5**, 202.
[16] *Nature*, May 20, 1933, 724.
[17] *Nat. Petr. News*, August 9, 1933, 24.
[18] *C.R.*, Nov. 27, 1933; *Nature*, Jan. 13, 1934, 75.
[19] *Ind. Eng. Chem.*, 1933, **25**, 1359.

with quartz windows in the cylinder. The presence of formaldehyde in the unburnt gases ahead of the flame front has been established when the engine is running under detonating conditions. Steele[20] describes observations on infra-red radiation from the cylinder of a gasoline engine fitted with a fluorite window. Morley[21] discusses the factors involved in knock-rating tests, particularly with regard to aviation gasolines.

Serruys[22] finds that the time during which detonation lasts in a single cycle is of the order of $1{\cdot}0 \times 10^{-4}$ second, and that the pressure rises to about 100 kgm./cm.^{2}, while a rise of about 100° C. in the temperature of the burning gases takes place during detonation. Dumanois[23] mentions some curious results on elimination of detonation by increasing compression ratio at high cylinder temperatures.

Taylor[24] discusses the mechanism of detonation, and concludes that knocking is caused by auto-ignition of the last part of the charge to burn, as originally suggested by Ricardo. The occurrence of detonation is believed to depend upon the auto-ignition temperature and the time lag of the last portion of the charge to burn. The rate and magnitude of the pressure rise determine the severity of detonation.

The measurement of detonation by means of observations on the rise in temperature of the cooling water during knocking has been described by Dumanois.[25] The method has been employed in the Series 30 engine, and also in an aircraft engine of 250 h.p. The rate of flow of cooling water through the cylinder jacket is adjusted so that there is a difference of 7° or 8° C. between inlet and outlet water readings. Fuels are rated for detonation by comparing their temperature rises with those of sub-standard blends of slightly higher and lower anti-knock values. The knock rating, in terms of the equivalent sub-standard fuel blend is calculated as arithmetically proportional to the temperature difference readings on the fuels. The results of the thermal method in the Series 30 engine generally agree with those obtained with the bouncing-pin.

The work carried out in recent years in Germany on combustion, flame travel and spontaneous ignition temperatures of fuels in

[20] *Ind. Eng. Chem.*, 1933, **25**, 388.
[21] *Aircraft Eng.*, June, 1933, 132.
[22] *Brit. Chem. Abs.*, April 14, 1933, 293.
[23] *C.R.*, July 31, 1933, 393.
[24] *Aircraft Eng.*, June, 1933, 136.
[25] *Proc. World Petr. Congr.*, 1933, **2**, 206.

relation to detonation is summarised by von Philippovich[26] and Schäfer.[27]

With regard to aviation gasolines, an important development is the adoption of the C.F.R. engine as the standard knock-testing engine by the British Air Ministry and by the aircraft manufacturers and users in the U.S.A. The use of the C.F.R. engine is prescribed in connection with the new fuel specifications DTD. 224 and 230 issued by the Air Ministry and already mentioned earlier in this report. The method of test is that of the C.F.R. motor method, except that a mixture temperature of 260° F. is employed instead of 300° F. The experimental work leading to the adoption of this method of knock testing is described by Pye,[28] the Chairman of the I.P.T. Committee responsible for the investigation. A number of straight aviation gasolines and benzol blends were tested for knock rating against mixtures of ethyl fluid in a standard fuel, using three single-cylinder units of aircraft engines, namely, one water-cooled and two air-cooled units. In the water-cooled engine tests were carried out at low and high air-intake temperatures, the latter representing supercharged conditions. In one of the air-cooled units tests were done both under atmospheric pressure and with supercharge. The method of working in the water-cooled and one of the air-cooled engines was to use full throttle, maximum detonation mixture strength and to find a standard fuel/lead mixture giving incipient detonation at the same engine speed as each unknown fuel. The compression ratio of these engines was varied in stages in order to bring the incipient detonation speed of all the fuels within the working speed range of the engines. In the second air-cooled engine tests were done both with throttling at constant speed and also by supercharging to the point of incipient detonation. It was found that the most severe conditions of test were those of supercharging and throttling. The knock ratings (in terms of lead and the standard fuel) of the fuels under these conditions of test were found to agree closely with those of the C.F.R. motor method when the mixture temperature was reduced to 260° F., and also with those of the Series 30 engine at 900 r.p.m. and 212° F. cylinder jacket temperature.

A paper by Cummings,[29] which represents a progress report of the Aviation Detonation Sub-Committee of the C.F.R. Committee, gives the history of the development of the knock testing of aviation gasolines in the U.S., including the work of the

[26] *Proc. World Petr. Congr.*, 1933, **2**, 210.
[27] *Proc. World Petr. Congr.*, 1933, **2**, 218.
[28] *Proc. World Petr. Congr.*, 1933, **2**, 186.
[29] *Proc. World Petr. Congr.*, 1933, **2**, 193.

U.S. Army Air Corps and that of certain American aircraft engine makers and oil companies. The current method used by the Army Air Corps involves the C.F.R. engine fitted with a special cylinder similar to that of the Series 30 engine. The test conditions specify 1200 r.p.m., 330° F. cylinder jacket temperature, full throttle and the use of a temperature plug for observation of detonation. Knock ratings are expressed in terms of concentration of lead tetraethyl in a straight-run aviation gasoline. The Aviation Sub-Committee of the C.F.R., which includes representatives of the aircraft and oil industries, has arranged a test programme for determining the best methods of measuring the knock rating of aviation gasolines. Tests on full-sized aircraft engines, in which detonation ratings observed by measuring cylinder temperatures will be compared with those of single-cylinder engines, such as the C.F.R., in order to decide on the conditions required in the latter to reproduce ratings in the aircraft engines. In the meantime the C.F.R. motor method has been temporarily adopted by the committee for testing aviation gasolines.

Work carried out at the D.V.L., Berlin, on the correlation of the results of the Armstrong knock-testing engine with those of a B.M.W. aircraft engine are described by von Philoppovich.[29] Power output, as shown by engine speed, cylinder temperature and, to some extent, appearance of the exhaust gases, were found to be the best indicators of knocking in the B.M.W. engine.

Development work on direct injection, spark-ignited engines for aviation is apparently still going on. In this type of engine fuels of low volatility, distilling between 100° and 200° C., are used with the object of decreasing fire risk. Fuels of this type cannot be vaporised at the induction temperatures of aircraft engines. The carburettor is consequently eliminated and the fuel injected by pump direct into the cylinder. Tests on this type of engine are described by Schey and Young,[30] who used a hydrogenated fuel having a flash point of 125° F. (compared with −30° F. for aviation gasoline). Using a supercharge pressure of 2 in. mercury and a compression ratio of 7 : 1, a B.M.E.P. of 175 lb./sq. in. was obtained with the "safety fuel."

Vapour Lock and Volatility.

The valuable work of Bridgeman and his collaborators at the Bureau of Standards, Washington, on vapour lock has been continued during 1933 in the direction of studying[31]

[30] National Advisory Committee for Aeronautics (U.S.A.) Report No. 471.
[31] *S.A.E.J.*, April, 1933, 157; *A.P.I. Proc.*, Oct., 1933, Sect. III., 18.

the vapour-handling capacity of automobile fuel systems. Road tests on 46 cars were carried out under various conditions and the temperatures of vapour lock in the fuel system were recorded. The fuels were prepared by adding butane to low vapour-pressure gasoline, the vapour pressures employed being from 12 to 27 lb. Reid at 100° F. It was observed that the vapour-locking temperature, *i.e.*, the temperature in the fuel line when loss of power first occurred or when the engine stopped on idling, was generally considerably higher than the vapour-locking temperature calculated on the assumption that the ratio of vapour to liquid volume was 1, when vapour lock took place. The discrepancy was particularly large in the case of engines provided with fuel pumps which are capable of handling larger volumes of vapour than are gravity-feed and vacuum-tank systems. The vapour-handling capacity of a fuel system is defined as the ratio, V/L of vapour to liquid in the system when vapour lock occurs. For each gasoline examined, curves were determined in the laboratory to show the relation between V/L and temperature at atmospheric pressure, *i.e.*, the temperatures at which the vapour pressure was atmospheric at different vapour/liquid volumes were measured. By means of these curves the value of V/L corresponding with the vapour-lock temperature of a fuel observed on the road could be deduced. The value of V/L for most of the (American) cars tested was between 10 and 30, but nearly 25 per cent. of the cars gave a value of less than 10, and 20 per cent. did not show vapour lock until V/L was greater than 30. Observations on fuel-line temperatures of the cars tested were also recorded, and it was found that for idling conditions the fuel temperature was, on the average, 33° F., and for steady running at 40 m.p.h. 20° F. above atmospheric temperatures, which varied between 73° and 97° F.

An article by Ainsley, Baker and Phillips[32] describes methods of testing vapour lock on the bench and road. Measurements of fuel-line temperatures under various conditions of driving at air temperatures from 40°–100° F. are recorded.

A method of measuring temperature drop when a fuel/air mixture is sprayed from a jet is described by Clothier[33] in connection with carburettor freezing.

The carburation of ethyl alcohol is discussed from the thermal point of view by Small.[34] The performance of methyl alcohol, and of fuels containing it, is dealt with by Howes.[35]

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[32] *A.P.I. Proc.*, Oct., 1933, Sect. III., 22.
[33] Aero. Research Comm. Rpts. and Memos., 1933, No. 1549.
[34] *Phil. Mag.*, Sept., 1933, 641.
[35] *J. Inst. Petr. Techn.*, 1933, **19**, 301.

Experiments to compare the ease of starting of gasoline, benzole and gasoline/benzole mixtures have been carried out by Hoffert and Claxton,[36] using a four-cylinder engine mounted on a test bed. The number of revolutions required to start the engine at various temperatures and air/fuel ratios were measured and the ease of starting taken as inversely proportional to the number of revolutions. The rate of motoring of the engine, which was between 150 and 210 r.p.m., was found to have no appreciable effect on the ease of starting. It was found that benzole gives easier starting than motor gasoline between 10° and 20° C., but as the temperature falls below 10° C. the ease of starting with benzole falls off more rapidly than with gasoline. Blends of benzole and gasoline gave startability intermediate between those of the constituents at temperatures of 10°–20° C., but from 0° to 10° C. certain benzole blends were superior to both constituents. Benzole and benzole/gasoline blends show a wider range of mixture strength than gasolines at which starting is possible. It was found that the startability results of gasolines on the English market could not be predicted from the distillation curves.

Engine-starting tests are also described by Wawrziniok.[37] The conclusion was reached that normal fuels have little effect on the starting of a correctly adjusted engine. Alcohol/gasoline mixtures containing up to 30 per cent. alcohol were found to be as good as gasoline for ease of starting, and even better than some gasolines at low temperatures.

Experiments with cars on a chassis dynamometer to examine the effect of gasoline volatility on engine economy and performance have been carried out by MacCoull.[38] It was found that a rise of 100° F. in the mixture-temperature, due to increased heating of the induction system, over the minimum required for good distribution, may produce a loss of 13 per cent. in power output and raise the anti-knock requirement of the fuel by 10 octane numbers. The performance of the average American engine with regard to power and acceleration is not much affected by fuel volatility within the range of fuels investigated, which distilled 30–70 per cent. to 100° C. and had end-points from 155° to 220° C. Fuel consumption improves with decreasing volatility of the fuel, but the improvement is small in comparison with the sacrifice involved in ease of starting. With the carburettor set to deliver a lean mixture, mileage per gallon increases with volatility of the fuel. With rich settings, which are normally employed on production

[36] *Engineering*, 1933, **155**, March 17, 300; April 7, 374.
[37] *Auto. Zeit.*, 1933, Sept. 25, 464; Oct. 10, 496.
[38] *S.A.E.J.*, Nov., 1933, 363.

engines, mileage increases with decreasing volatility of the gasoline. By using the least induction manifold heat which is required for good distribution and the highest compression ratio possible without detonation, greater power and fuel economy can be obtained with increased fuel volatility.

The relationships between volatility, as shown by the distillation curve, and engine performance are discussed by Brown,[39, 40] and Oberfell and Alden.[41]

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[39] *Oil & Gas J.*, Jan. 19, 1933, 13.
[40] *Oil & Gas J.*, May 18, 1933, 51.
[41] *Oil & Gas J.*, Jan. 19, 1933, 14.

Kerosine and White Spirit.

By J. S. Jackson, B.Sc., A.I.C. (Member).

There has, perhaps, been a tendency in recent years to assume that Kerosine and White Spirit should not attract a great deal of attention. This attitude is rather surprising in view of magnitude of kerosine sales both at home and abroad. One often hears the statement that the kerosine market is a dying market. Whatever measure of truth there may be in this statement the fact remains that over the last five years even in Great Britain the kerosine imports and home production have amounted to approximately 10 per cent. of the total imports and home production of petroleum and its products. This figure compares with 5 per cent. approximately for lubricating oil.

There are now interesting indications that the use of kerosine for heating purposes is steadily increasing. As a result of this development the market has become more critical and its requirements are more varied and at the same time more precise.

The increased interest in kerosine for heating purposes is evidenced by the many patents granted for improved kerosine burners.

Curiously enough, the increased use of kerosine for heating purposes seems to have resulted in renewed interest in the refining of kerosine for illuminating purposes.

N. Danaila[1] has carried out further work of interest on a range of Rumanian kerosines. He has shown that all kerosines containing a definite percentage of aromatics give higher candle powers than the corresponding aromatic-free burning oils. He, therefore, favours those refining methods which remove only tarry and sulphurous constituents, leaving the aromatic bodies more or less unaffected.

E. Saegebarth[2] has patented an improved method for the treatment of moisture-containing liquid hydrocarbons with liquid SO_2.

The first stage extract evaporation is conducted at condenser pressure, the SO_2 being dried and added to the undried SO_2 evolved from the other stages. In this way the accumulation of water in the treatment cycle is prevented. A similar patent has been obtained by the Edeleanu G.m.b.H.[3] This invention also aims at removing any water which may collect in the system.

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[1] *Petr. Zeit.*, 15.2.33, **29** (7), 1-5.
[2] U.S.P. 1,917,736, 11.7.33.
[3] E.P. 391,308, 27.4.33.

H. S. Garlick[4] in a general survey of the development of hydrogenation as applied to petroleum refers to the conversion of heavy kerosines into oils of excellent burning properties by means of hydrogenation.

The nitrogen compounds occurring in kerosines have been studied in connection with colour stability problems and in this connection T. S. Perrin and J. R. Bailey[5] have described a method of isolating such nitrogen compounds from kerosine distillates.

Several papers presented at the World Petroleum Congress dealt with kerosine, various problems arising in connection with colour stability having received particular attention. L. P. McHatton[6] dealt with the Discolouration of Colour Unstable Kerosines. He described the types of discolouration which can be faded by exposure to sunlight, reappearing in the dark. This discolouration he attributed to (*a*) phenols; (*b*) hydrocarbons resembling cyclopentadiene derivatives and (*c*) unidentified hydroxyl compounds.

B. H. Moerbeek[7] dealt with the problem of discolouration in a more general manner and described tests by which colour instability may be predicted. The causes of discolouration are described and the PbO_2 test devised by Hillman is stated to be a very satisfactory test which need only be supplemented by a test for nitrogen bases such as the silico-tungstic acid test. The preparation of PbO_2 from lead tetra-acetate is recommended.

E. S. Hillman[8] who devised the PbO_2 test, described in detail the actual problem of refining kerosine to a colour-stable product. The application of the PbO_2 test is also described. This work marks a very distinct advance in the control of the available refining methods.

This important problem of colour stability was also dealt with by B. C. Allibone[9] with special reference to the conditions prevailing in India. The use of sulphur dioxide extraction in conjunction with a finishing bauxite filtration is recommended.

In a second paper B. H. Moerbeek[10] summarised the properties that a lamp kerosine should possess to satisfy the requirements of the public.

The standardization and publication of the Smoke Point Test marks a very important advance in the testing of kerosines.

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[4] *Ind. Chem.*, 1933, **9**, 226–227.
[5] *J.A.C.S.*, 1933, **55**, 4136–4140.
[6] *Proc. World Petr. Congr.*, 1933, **2**, 721.
[7] *Proc. World Petr. Congr.*, 1933, **2**, 713.
[8] *Proc. World Petr. Congr.*, 1933, **2**, 708.
[9] *Proc. World Petr. Congr.*, 1933, **2**, 725.
[10] *Proc. World Petr. Congr.*, 1933, **2**, 703.

B. H. Moerbeek[11] described the general experimental basis of the test while W. A. Woodrow[12] dealt with the development of the published I.P.T. method. This test possesses many of the characteristics of an ideal test. It is simple, accurate and practical, and must, therefore, be of great value.

A description of the standard Smoke Point Method was published in the September issue of the journal of this Institution.[13]

J. S. Jackson[14] in his paper on the "Testing of Kerosine for Illuminating Purposes" described a development of the 24-hr. burning test in which the weight of dry char formed provides a measure of all the undesirable constituents of the kerosine.

He also emphasised the importance of evolving a Long-Burning Test by which the luminosity of the flame as well as the flame dimensions could be studied and controlled.

The testing of "Kerosines for Power Purposes" was dealt with by R. Stansfield and A. R. Stark[15] who stated that for these kerosines three tests only were essential; the Octane Number determined by the C.F.R. Motor Method, the distillation by the I.P.T. Method for kerosines and a test for corrosive sulphur.

The above publications provide convincing indications that progress has been made in connection with the manufacture and use of kerosine during the past year. There will obviously always be a considerable demand for kerosine as an illuminant and there are unmistakable signs that increased quantities of kerosine are being used for domestic cooking and heating purposes. Kerosine is the heaviest petroleum distillate which can at present be readily and satisfactorily vaporised and it must necessarily be more and more widely used in the increasingly popular oil-fed cookers, heaters and radiators.

White Spirit.

The suggestion has been made by C. I. Kelly[16] that petroleum white spirit might be improved by the addition of aromatic hydrocarbons synthesised from petroleum gases or by the production of naphthas of superior solvent properties by hydrogenation processes.

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[11] *Proc. World Petr. Congr.*, 1933, **2**, 730.
[12] *Proc. World Petr. Congr.*, 1933, **2**, 732.
[13] *J. Inst. Petr. Techn.*, 1933, **19**, 812–814.
[14] *Proc. World Petr. Congr.*, 1933, **2**, 699.
[15] *Proc. World Petr. Congr.*, 1933, **2**, 706.
[16] *J. Oil Colour Chem. Assoc.*, 1933, **16**, 95–127; *Oil and Colour Trades J.*, 1933, **83**, 715–720.

Lubricants and Lubrication.

By A. R. Bowen, D.Sc., Ph.D., F.I.C., A.M.I.Chem.E. (Member).

In the past year an increasing interest has been shown in the production of the best quality of lubricant possible from the raw materials available. The recent symposium of the American Petroleum Institute has included descriptions of a number of new solvent refining processes which will doubtless be described more fully elsewhere in these reports, but of which mention must be made here. These solvent extraction processes separate a lubricating oil into high and low grade fractions, and among the solvents put forward are nitrobenzene,[1] $\beta\beta'$-dichloroethyl ether[2] and phenol[3]; furfural has also been suggested. Phenol-treated oils have been marketed in this country to a small extent and have met with considerable success. The Duo-Sol[4] process uses two immiscible solvents with which to treat a lubricating oil distillate, the solvents being liquid propane, which is the selective solvent for the paraffin-type constituents, and a special blend of coal-tar acids and bases being the solvent for the naphthenic-type constituents. Many modifications of normal refining procedure at once become possible. The addition of liquid propane would cause asphalt precipitation, and evaporation of propane would supply the necessary chilling for de-waxing,[5] and, by using an excess of propane over that required for refrigeration, a wax-precipitating medium of great efficiency is provided. The Edeleanu Process[6] has also been further investigated with regard to the improvement of lubricating oils. The use of acetone extraction of lubricating oils with its effect on friction[7] characteristics has been the subject of a recent investigation.

Hydrogenated lubricating oils have appeared on the British market during this last year, and on account of their good viscosity-temperature index and high degree of chemical stability have become unquestionably popular. Certain experimental work on the refining of hydrogenated lubricating oils suggesting the use of

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[1] S. W. Ferris and W. E. Houghton, *Oil & Gas J.*, 17.11.32, **31** (26), 65; *Refiner*, 1932, **11**, 560.

Note.—The principles of Solvent Extraction Processes have been described by T. G. Hunter and A. W. Nash, *Proc. World Petr. Congr.*, 1933, **2**, 340.

[2] J. M. Page, C. C. Buchler and S. H. Diggs, *Ind. Eng. Chem.*, 1933, **25**, 418.

[3] R. K. Stratford, *J.S.C.I.*, 1933, **52**, 266; *c.f. Nat. Petr. News*, 29.3.33, **25** (13), 17.

[4] M. B. Miller, *Oil & Gas J.*, 1933, **32** (21), 11; *Nat. Petr. News*, **25** (41), 26.

[5] W. H. Bahlke, R. N. Giles and C. E. Adams, *Refiner*, 1933, **12**, 229; R. C. Conine, *Oil & Gas J.*, 4.5.33, **31** (50), 11.

[6] W. Kain, *Refiner*, 1932, **11**, 553; *c.f.*, O. P. Cottrell, *Oil & Gas J.*, 1.12.32, **31** (28), 10.

[7] M. Nottage, *J. Inst. Petr. Techn.*, 1932, **18**, 943.

Japanese acid clay has been put forward by Y. Tanaka, R. Kobayashi and A. Misono.[8]

Lubricating oils[9] of high viscosity and low setting point are stated to be formed by thermal dechlorination of chlorinated paraffin wax. This mode of synthesis would appear to merit further investigation.

The synthesis of viscous hydrocarbons, described recently,[10] provides valuable material to be added to the scanty facts known on such hydrocarbons. It is only when much more is known of pure hydrocarbons prepared synthetically that progress will be made on the determination of the hydrocarbons present in petroleum lubricating oil fractions. In the work mentioned, certain dialkyl-dihydroanthracenes were found to be very viscous liquids at ordinary temperature, but whose viscosity falls off very sharply on heating. A number of branched chain olefines and paraffins containing up to 48 carbon atoms were also prepared. These liquids have much lower viscosities than the cyclic compounds, for example, the methyl-β-octyl tetracosylene ($C_{32}H_{64}$) having a viscosity of 0·176 poises at 24° C. and dimethyl-tetrahexyl docosane ($C_{45}H_{98}$) having 1·61 poises at 25° C. An announcement[11] has been made that the U.S. Bureau of Standards intend to isolate lubricating oil hydrocarbons.

Further interesting experiments[12] have been carried out on the effect of paraflow on lubricating oils, and its action of lowering the setting point has been shown to vary from oil to oil. For heavier oils such as aircraft oils, the addition of paraflow is stated to have no effect.

Colour reversion properties of lubricating oil distillates from a Burmah crude oil have been described by A. R. Bowen.[13] When certain temperatures are reached in distillation, that is when restricted amounts of steam or low vacua are used, the distillates show both types of reversion: polymerisation (dark reversion) and oxidation (sunlight reversion).

Interesting laboratory experiments[14] have been described comparing steam and natural gas as distillation media for petroleum products. A number of experimental studies have been described

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[8] *J. Soc. Chem. Ind.*, Japan, 1933, **36**, 227B.
[9] Y. Tanaka, R. Kobayashi and H. Furumoto, *J. Soc. Chem. Ind.*, Japan, 1933, **36**, 228B, *c.f.* E.P. 396,147.
[10] M. Lerer, *Ann. des Comb. Liq.*, 1933, **8**, 681.
[11] *Nat. Petr. News*, **25** (51), 29.
[12] H. Suida and H. Pöll, *Petr. Zeit.*, 7.6.33, **29** (23), *Motorenbetrieb*, **6** (6) 2; *c.f.*, P. M. Robinson, *Refiner*, 1933, **12**, 273.
[13] *J. Inst. Petr. Techn.*, 1933, **19**, 364.
[14] G. Allen and F. T. Gardner, *Oil & Gas J.*, 4.5.33, **31** (50), 12.

on viscosity, including :—the theory[15] of laminar flow at the entrance of an Engler viscosimeter tube, approximate calibration[16] of apparatus for measuring absolute viscosity, kinematic[17] viscosities and times of outflow from commercial viscosimeters and a suspended level viscosimeter.[18] Other subjects bearing on analysis that have been under review during last year, which will be dealt with more fully in the reports on that subject, are : demulsification, ultra-violet radiation tests, photo-electric colorimeter and the analytical steam distillation of lubricating oils.

High-pressure capillary flow has been investigated by M. D. Hersey and G. H. S. Snyder.[19] This work deals with the flow of liquids through capillaries under inlet pressures so high that the viscosity cannot be assumed to be uniform throughout the length of the tube. The change in the viscosity of oils with temperature is continually under review with regard to the best method for its expression. The importance of the slope of the viscosity-temperature function for the evaluation of lubricating oils has been stressed again by H. Umstätter.[20] In discussing the viscosity index and other properties of Pennsylvania oils, M. R. Fenske[21] states that high vacuum fractionation of a number of such oils shows the fractions to have a very uniform and regular variation in properties as the boiling point increases. It is suggested that this investigation indicates the desirability of the development of solvent-extraction processes to produce from these oils the closer "fractionation" which is necessary to improve such properties as viscosity index.

T. O. Bell and L. H. Sharp[22] have presented a practical viscosity-temperature coefficient for oil products, which is claimed to be superior to other systems in that it indicates not only the change of viscosity with temperature, but permits calculation of viscosity at any given temperature, and, being approximately additive, the coefficient of a blend can be predicted from its components. Again, the viscosity-temperature zone-gravity classification of lubricating oils has been discussed by C. M. Larson and W. C. Schwaderer.[23] The Dean and Davis and Larson and Schwaderer systems for the determination of viscosity index of a lubricating oil are discussed.

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[15] L. Schiller, *J. Rheo.*, 1932, **3**, 212.
[16] C. H. Weiss and M. Louis, *J. Rheo.*, 1932, **3**, 217.
[17] F. H. Garner and C. I. Kelly, *Physics*, 1933, **4**, 97.
[18] L. Ubbelohde, *J. Inst. Petr. Techn.*, 1933, **19**, 376 ; *c.f.* M. Louis and M. Peyrot, *Ann. des Comb. Liq.*, 1932, **7**, 1055.
[19] *J. Rheo.*, 1932, **3**, 298.
[20] *Petr. Zeit.*, 9.8.33, **29** (31), 1.
[21] *Nat. Petr. News*, 5.7.33, **25** (27), 33.
[22] *Oil & Gas J.*, 17.9.33, **32** (13), 13.
[23] *Nat. Petr. News*, 10.5.33, **25** (19), 26.

It is pointed out that while evaluations made by the Dean and Davis system are not constant throughout the temperature range of the A.S.T.M. viscosity-temperature chart, evaluations made on the Larson and Schwaderer system are constant. A conversion chart is given for the two systems, and the new viscosity index chart is reproduced.

An ingenious method for the estimation of the alteration of oils by heat, ultra-violet radiation or actual use in an engine, is described by J. J. Trillat and L. Leprince-Ringuet,[24] who noted the change in interfacial tension between the oil and pure water, the du Noüy apparatus being used. The relation of the lubricant and fuel to the carbon formation in an engine has often been the subject of discussion. P. W. Stroud[25] points out that although gasolines containing high proportions of gum can be the main cause of damage in an engine, yet the lubricating oil should be considered as regards carbon-forming tendencies. That heavy residual oils are the main lubricating components of motor oils is the subject of a paper by P. M. Robinson,[26] who states that they contain more "polar bodies" than distillate oils. Higher fatty acids of the stearic acid type have been found in the naphthenic acids separated from a spindle oil distillate.[27] Engine results using synthetic lubricating oils have been reported by D. P. Barnard,[28] and olefine-polymer oils were characterised by somewhat higher consumption than ordinary oils, but it was noted that the condition and properties of the synthetic oil after test was much superior to that of the conventional type oils.

R. C. Conine[29] has raised the question of lubricated gasoline. Opinions on the value of adding small percentages of light lubricating oils to gasoline for top cylinder lubrication are divided. Very few of the expected advantages of such an addition to gasoline have been noticed, though advantage may accrue when new engines are being run in. Some special lubrication problems have been discussed, recently, regarding vertical journal bearings[30] (such as are used in deep-well pumps), wire ropes,[31] and metal working.[32]

Three recent papers provide useful information of a practical

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[24] *Ann. des Comb. Liq.*, 1933, **8**, 492.
[25] *Oil & Gas J.*, 6.4.33, **31** (46), 12.
[26] *Nat. Petr. News*, 5.7.33, **25** (27), 29.
[27] E. Holzmann and S. v. Pilat, *Brenn. Chem.*, 1933, **14**, 263.
[28] *Nat. Petr. News*, 16.11.32, **24** (46), 62.
[29] *Oil & Gas J.*, 29.12.32, **31** (32), 9.
[30] A. I. Ponomareff and E. D. Howe, *Trans. A.S.M.E. Petr. Mech. Eng.* 31.5.33, **55** (6), 27.
[31] A. J. Morgan, *Power*, 1933, **77**, 430.
[32] *Chem. Trade J.*, 1933, **93**, 211.

character. W. H. Graves[33] has discussed oil consumption in motor-car engines showing it to be dependent on three main factors: engine speed, engine design and changes due to wear, and oil characteristics. These are treated in more detail. With regard to the latter, data are given to show conclusively that as viscosity of the lubricant increases, the oil consumption decreases up to a critical viscosity, after which oil consumption increases with increase in that property; the probable reason for this is suggested. Work by various investigators demonstrates that volatility is an important factor as regards oil consumption. The paper of A. L. Clayden[34] reviews the possible general modifications in engine design which would have the effect of lessening the burden now placed on the lubricant, and this is discussed under the headings: oil wastage, bearing lubrication and oil deterioration. In a paper on aircraft engine lubrication,[35] A. Nutt points out that the selection of oils is based on operating experience on the basis of which attempts have been made to prepare purchasing specifications. Oils passing such specifications have on occasions proved unsuitable in use. It is recommended that the selection of an oil should be made from the result of actual testing in an engine over a period of time. Oils of mineral origin with as flat a viscosity-temperature curve as possible and low pour test are desirable for this purpose.

An account of some recent advances in the applications of greases in industrial lubrication problems has been made by H. S. Garlick.[36] Compounds consisting of an aluminium soap emulsified with a medium motor oil are known as "lucid" compounds on account of their appearance. Such compounds are discussed by C. H. Kopp,[37] who remarks on their extreme stringiness, adhesiveness and limpidness. Stringiness and adhesiveness can be secured by the addition of aluminium oleate among other substances. These greases are easily decomposed by water vapour, and this limits their field of application and bars them from, for example, automobile differentials and transmissions or free-wheeling units. F. J. Licata[38] has described the effect of the rate of cooling in the manufacture of aluminium stearate greases. In lubrication by soda-base greases, F. H. Rhodes and H. D. Allen,[39] point out that the soap plays an important part in the formation of the lubricating film. The greases in question were prepared by dissolving fat

[33] *A.S.T.M.*, Symposium on Motor Lubs., 1933, 85.
[34] *A.S.T.M.*, Symposium on Motor Lubs., 1933, 101.
[35] *A.S.T.M.*, Symposium on Motor Lubs., 1933, 114.
[36] *Chem. Trade J.*, 1933, **92**, 236, 258.
[37] *Petr. Eng.*, 1932, **4** (1), 84.
[38] *Nat. Petr. News*, 7.6.33, **25** (23), 23.
[39] *Ind. Eng. Chem.*, 1933, **25**, 1275.

in petroleum oil and then heating the mixture with strong caustic soda solution until the fat had saponified and almost all the water was driven off. These products contain mixtures of sodium soaps of various fatty acids in varying proportions. The presence of sodium oleate in solution in the oil is stated to decrease the coefficient of static friction. The glycerol is considered to stabilise the grease and minimise the change in consistency on heating or in use, increasing also the lubricating power and eliminating the increase in the coefficient of static friction. E. W. Nelson[40] has described the determination of the consistency of fluid and semi-fluid greases by the Gardner Mobilometer, while a falling-sphere viscometer test and a " string " test are described for the consistency control of soft and stringy greases by E. R. Lederer and E. W. Zublin.[41]

The effect of sodium and ammonium soaps in producing lubrication during wire-drawing through a specially designed apparatus has been studied by R. C. Williams.[42] The effective lubricating properties of sodium and ammonium soap solutions were due to the products of hydrolysis, namely, fatty acids or acid soap.

Extreme pressure lubricants have received the attention they merit, and important communications have appeared in the literature. W. T. Sieber[43] points out that the use of extreme pressure lubricants has become necessary since the introduction of hypoid and worm-gear drives for modern automobile transmission. There are three main types of oil : petroleum oil blended with a saponifiable oil that has been treated with sulphur chloride ; petroleum oil blended with a saponifiable oil to which elementary sulphur has been added ; lead soap lubricants to which sulphur has been added or in which sulphur occurs naturally in the petroleum oil used. Saponifiable oils of mineral origin are generally used, but vegetable oils may be employed. In sulphurising these fatty compounds great care must be exercised in order to combine the sulphur or chlorine in the right way to obtain maximum pressure stability with minimum corrosion tendency. This is fairly simple to accomplish with the use of sulphur chloride, provided the finished compound is freed from hydrogen chloride formed during the reaction. Owing to difficulties in handling, however, few manufacturers use sulphur chloride. Saponifiable oils are generally sulphurised with the aid of flowers of sulphur at high temperatures, the process requiring considerable time and

[40] *Nat. Petr. News*, **25** (40), 25.
[41] *Nat. Petr. News*, **25** (37), 36.
[42] *J. Phys. Chem.*, 1932, **36**, 3108.
[43] *Petr. Eng.*, 1933, **4** (13), 22 ; *c.f.* O. C. Bridgeman, *Oil & Gas J.*, 17.11.32, **31** (26), 50.

care. Efficient ventilation is necessary to remove the large quantities of hydrogen sulphide liberated.

One factor of importance in the manufacture of lead soap lubricants is the necessity to incorporate the soaps with mineral oil at a temperature of approximately 400° F. in order to obtain maximum pressure stability. Many varieties of petroleum oil are used, but it is essential to employ a well-refined oil to avoid undue increase in viscosity and consistency of the lubricant owing to oxidation.

The evolution of a satisfactory laboratory method for determining the performance of extreme pressure lubricants is a subject on which some valuable research has been reported. H. R. Wolff and H. C. Mougey[44] describe recent work in this connection. Sulphur and chlorine are the most effective additive agents in use at present. Lead soaps require the addition of free or loosely combined sulphur in order to be effective, and they tend to precipitate from the oil and to form a lead sulphide sludge with the sulphur present. Reference is made to a number of laboratory testing machines which have been proposed, and the fallacy of accepting such machines as a primary standard for evaluating lubricants is pointed out. Performance in actual service must be the primary standard, and the test method standardised in terms of primary service data. However, it is difficult to obtain such data at present, since few automotive manufacturers are marketing products which require extreme pressure lubricants. The large machine described by Mougey and Almen was found to give unsatisfactory correlation, and a new one has been designed which is portable and less expensive. This is known as the "Almen Extreme-Pressure Lubricant Testing Machine," and several models have been built and are being used by members of the S.A.E. Lubricants Research Committee for research work. A description is given of the machine and of the operating conditions which appear to give the best correlation against service data on rear axles employing steel on steel spiral bevel or hypoid gears. Analyses of a number of extreme pressure lubricants are quoted, and results are given of actual service tests which were carried out on many of them in cars and trucks of current production. Practically all such lubricants will oxidise and thicken when high temperatures are encountered. The copper strip test is shown to be useless as an indication of corrosive properties of the lubricant in use. Two instances of corrosion when using sulphur chloride extreme pressure lubricants are reported and believed to be due to contamination with water in service. The co-operation of the Petroleum and

[44] *Oil & Gas J.*, 17.11.32, **31** (26), 58.

Automotive Industries is required in order to solve the related problems of gear development and extreme pressure lubricant manufacture.

An apparatus for finding the load-carrying capacity of extreme pressure lubricants has been described by S. A. McKee, F. G. Bitner and T. R. McKee.[45] The apparatus consists essentially of two self-aligning steel rolls made of fine-grain nickel molybdenum steel, about 2 in. in diameter and ½ in. wide, acting under load and mounted so that each could be driven independently at various speeds. Their working surfaces are true cylinders, but their bores are ground on a taper. The machine contains two interconnected sets of gears mounted on anti-friction bearings in individual oil-tight cases.

S. A. McKee, E. A. Harrington and T. R. McKee[46] state further that several laboratory machines and test methods have been developed for the determination of the properties of a lubricant that are measures of its service performance. Four of these machines for measuring the load-carrying capacity of extreme pressure lubricants were selected for examination by the U.S. Bureau of Standards. All the machines were used for observing the load necessary to produce seizure when applied to two steel surfaces rubbing together at constant speed and lubricated with the lubricant under test. The test procedures recommended by the makers of the machine varied in rubbing speed and one or two other points. Preliminary tests with nine widely different lubricants indicated a lack of agreement by the machines. Several alterations in test procedure were made, and the effects of speed and temperature were examined. It was found that: no set of operating conditions could be chosen for each machine, so that all the machines would rate all the lubricants in the same order; the load-carrying capacity of an extreme pressure lubricant tends to decrease as the temperature increases and tends to decrease as the rubbing speed increases; the effects of speed and temperature differ with the particular lubricant and machine involved to such an extent that even the order of rating may be changed; the ratio of the applied load to the actual pressure changes rapidly on running with each of the four machines, which throws serious doubt on the comparability of the data. A serious difficulty encountered with one machine was that rapid wear usually occurred under the conditions of operation necessary to approach the point of seizure, so that the area of contact increased and hence the pressure was continually changing. A new machine is being developed at the Bureau of Standards in which the ratio

[45] *Nat. Petr. News*, 6.9.33, **25** (36), 21.
[46] *J.S.A.E.*, 1933, **32**, 217.

of the applied load to the actual pressure will remain constant throughout each run. With the proposed machine, the speed and temperature may be changed over wide limits, and also the action between the surfaces under load may be changed as desired, from pure sliding to pure rolling, with various intermediate steps of combined rolling and sliding.

The "four-ball" testing apparatus for extreme pressure lubricants has been described by G. D. Boerlage.[47] This apparatus is stated to be simple and easy to manipulate, results being obtained rapidly and cheaply. A weighted belt-driven vertical shaft having a cup-shaped lower end rests on a $\frac{1}{2}$ in. diameter ball-bearing. This ball rests on three others arranged in the form of a pyramid, and the three balls are pressed tightly together by a conical ring, and on to the bottom of a cup which retains the oil under test and the balls. The upper ball therefore has three points of contact, one with each ball. The shaft is rotated and the friction of the balls tends to rotate the oil-containing cup which rests on a table supported on ball-bearings. The torque on this table is measured by a spring dynamometer.

The evaluation of extreme pressure lubricants by the Timken Tester has been discussed by A. P. Frame and A. K. Graham,[48] and the determination of lead in greases has been described by A. D. Bauer and C. S. Ford.[49]

Discussing the effect of viscosity on friction in the region of thin film lubrication, O. C. Bridgman, S. A. McKee and F. G. Bitner[50] describe experiments made with a modified Herschel "oiliness machine" designed to allow a wedging action in the oil film. For the four mineral oils used, all the experimental data fitted on one curve when the coefficient of friction was plotted against ZN—*i.e.*, viscosity (centipoises) x speed (r.p.m.). This curve is similar in shape to the individual friction speed curves, and indicates that in the thin film region of lubrication the coefficient of friction decreases as the viscosity is increased, the reverse being true in the region of thick film lubrication.

Other apparatus for testing "oiliness" has been described.[51]

A recent paper by R. O. King,[52] describing the beneficial effect of slight oxidation on the lubricating properties of oils, gives confirmation to the known fact that mineral oils in service lubrication conditions increase their content of polar bodies.

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[47] *Engineering*, 1933, **136**, 46.
[48] *Oil & Gas J.*, 5.1.33, **31** (33), 14.
[49] *Nat. Petr. News*, **25** (37), 37.
[50] *A.P.I. Proc.*, Sect. III, Dec., 1932, 154.
[51] *Oil & Gas J.*, 7.9.33, **32** (16), 10; *Automobile Engineer*, 1933, **23**, 427.
[52] *Proc. Roy. Soc.*, 1933, *A*, 139.

The reclamation of used oils has been described frequently and regeneration processes have been put forward. Oil reclamation economics have been discussed by G. T. Hook,[53] who reviews available information, chiefly in the form of reports from operators of large fleets of 'buses and haulage trucks, and decides that the effect of reclaimed oil on the engine is at least as good as, and not any worse than, that of the original oil.

Examples from operators using reclaimers are put forward which indicate that an overall cost of reclamation, including overhead, is about 12 cents per gallon, varying according to variable conditions from 10 to 18 cents.

E. Vellinger and A. Klinkenberg[54] suggest a physico-chemical method for determining the acidity of aged mineral oils.

The determination of the acidity of aged oils by the usual methods is difficult owing to the dark colour. The authors use the antimony electrode and titrate potentiometrically in alcohol-ether mixtures adding lithium chloride.

A number of patents have appeared during the year covering advances in production, refining, preparation and reconditioning of lubricants. Many of these show points of only minor novelty. The following are some of these processes and claims which are of interest.

Solvent extraction of lubricating oil distillates to separate the paraffinic and naphthenic-type constituents have been prominent among new refining processes. The following solvents[55] have been put forward : benzaldehyde, benzonitrile, aliphatic aldehydes such as propionaldehyde, ethylene glycol ethers and their acyl derivatives, phenol and polyhydric alcohol blends, wood tar acids and cresylic acid ; the two latter may be used with other solvents, *e.g.*, furfural and liquid propane.

For the production of light coloured lubricating oils, a process[56] has been suggested involving removal of moisture from the raw lubricating oil stock, air-blowing to oxidise the highly unsaturated constituents, then treatment with sulphuric acid and neutralisation.

In order to prevent deterioration of lubricating oils, W. Helmore and E. W. J. Mardles[57] suggest the addition of small proportions (less than 1 per cent. by weight) of metallic tin or an organic derivative of tin, *e.g.*, tin oleate, tin naphthyl, tin ricinoleate, tin

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[53] *J.S.A.E.*, 1933, **32**, 20 ; *c.f.* A. E. Mockler, *Oil & Gas J.*, 15.12.32, **31** (30), 28 ; D. H. Foster, *Nat. Petr. News*, 12.4.33, **25** (15), 66 ; *J. Inst. Auto. E.*, June, 1933, 73 ; *Nat. Petr. News*, 12.7.33, **25** (28), 29.

[54] *Ann. des Comb. Liq.*, 1933, **8**, 301.

[55] U.S.P.s 1,904,402 ; 1,899,969 ; (*c.f.* E.P. 383,801) ; 1,910,422 ; 1,908,018 ; 1,892,655 ; 1,912,348–9.

[56] U.S.P. 1,927,823.

[57] E.P. 398,222.

phenyl or tin methyl iodide. In addition to the tin compound, tetra-ethyl lead or lead oleate may also be added. The lubricating oil concerned may be a vegetable oil, such as castor oil, or a compounded vegetable and mineral oil.

The Timken Roller Bearing Co. describe[58] a machine for testing lubricants or the wear of materials. Stiff lubricants[59] are claimed by mixing a cellulose ether or ester in castor or sperm oils, together with a heavy mineral lubricating oil; and a gear oil has been described[60] which is composed of a major proportion of a heavy mineral oil and a minor proportion of a heavy unctuous synthetic material consisting of a condensation product (*e.g.*, reaction product of naphthalene and chlorinated paraffin wax in presence of aluminium chloride), to which mixture a metallic soap may also be added.

F. Hofmann and C. Wulff[61] have patented the production of viscous oils by the condensation of aromatic hydrocarbons together with olefines, with heating in the presence of a hydrogen halide and a halide of boron.

Oils of lubricating type are also claimed from: brown coal,[62] by treatment with a solvent such as xylene at elevated temperatures and under high pressures; from coal-tars, etc., and mineral oils by treatment[63] with an anhydrous metal halide or other condensing agent followed by non-destructive catalytic hydrogenation; and from tar oils[64] prepared by distilling coal, etc., at comparatively low temperatures by means of superheated water-gas.

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[58] E.P. 395,976.
[59] E.P. 398,936.
[60] E.P. 396,147.
[61] U.S.P. 1,933,434.
[62] U.S.P. 1,904,477.
[63] U.S.P. 1,914,727.
[64] U.S.P. 1,886,262.

Gas Oil, Diesel Fuel and Fuel Oil.

By C. G. Verver.

In the field of the heavy petroleum fuels, the subject to which the most attention has been devoted during 1933 was that of Diesel fuel oil. Although no startling developments appear to have occurred in the period, the number of high-speed Diesel engines for heavy vehicles has continued to increase rapidly, whilst the steady improvement in design has brought forth sweeping prophecies with respect to the future of this engine, one author even going so far as to state that "a Diesel car, . . . when it does appear, will be such an advance on modern performance of a petrol car that, with the exception, perhaps, of the high-powered luxury vehicle, all petrol cars will be automatically out of date."[1] It is consequently not surprising that active research is continuing in several centres on the evaluation of Diesel fuel and on methods for improving its quality.

As was pointed out by Stansfield,[2] a commendable restraint is being shown in the standardization of a method for testing the knocking propensities of a Diesel fuel. Apparently there is a desire to avoid a situation similar to the confusion created in the domain of gasoline knock-testing by the over hasty adoption of a standard procedure. In one respect the two cases are probably similar; whilst it is a relatively simple matter to rate "normal" (*e.g.*, straight-run mineral) fuels, the rating may become very complex when "modified" (such as doped or cracked) fuels enter the field. The present situation was dealt with by a number of the authorities on the subject in papers presented before the World Petroleum Congress in London during July, 1933.

The methods of judging Diesel fuels may be divided into five categories :—

(*a*) Methods involving a measurement of ignition delay;
(*b*) Methods designed to measure the "uncontrollable" pressure rise, which causes the knock;
(*c*) Starting tests, involving the determination of the compression ratio required to produce incipient combustion;
(*d*) The determination of the knocking properties of a petrol-Diesel fuel blend in a standard gasoline knock-testing engine;
(*e*) Self-ignition temperature tests.

Stansfield[3] has described the results of a series of experiments subsequent to the fundamental work carried out in the

[1] Goddard, *J. Inst. Petr. Techn.*, 1933, **19**, 885–917.
[2] Stansfield, *Proc. World Petr. Congr.*, 1933, **2**, 256.
[3] Stansfield, *loc. cit.*

Anglo-Persian laboratories.[4,5] Employing the cetene-α-methylnaphthaline scale developed by Boerlage and Broeze in the Delft laboratories of the Royal Dutch Shell Group,[6,7] the rating of a number of fuels according to method "*a*" in a Gardner engine was determined with a considerable variation of jacket and air temperatures. The mean variation in cetene number, as between 20° and 100° C., amounted to but ±4, which is relatively unimportant. Comparing the rating found with three different Diesel engines, Stansfield further found that the evaluation of the fuels tested by him agreed to within a value differing by the equivalent of 3 cetene numbers at most. He also described a number of starting tests carried out on the Gardner engine (*i.e.*, by a method of type "*c*"), whereby it was possible to rate the fuels to cetene figures agreeing to within 2 points of the values obtained by ignition lag measurement, the only irregularities being observed in the case of fuels doped with ethyl nitrate. Stansfield concluded that a starting method will be entirely suitable (and preferable owing to its simplicity) until the possible advent of temperature-sensitive fuels in commerce.

Boerlage and Broeze[8] give a description of their well-known method of measuring the delay in a Thomassen engine, and continue with an account of work done with a modified C.F.R. engine. With the latter equipment the ignition quality was judged either by measuring the vertical pressure rise (*i.e.*, a "*b*" method) or the delay period ("*a*"). A form of bouncing pin could be employed for both measurements, whilst the second was also estimated optically. Boerlage and Broeze also found that there is a good correlation between cetene numbers and the ignition quality as judged in four other engines, and hence agree with Stansfield that the rating of a Diesel fuel is (with certain reservations) relatively insensitive to engine design.

The two last-named authors further give an interesting account of a testing method falling under the group "*d*" in the list given above. The work was done partly by the Delft laboratory and partly by M. Dumanois in France. Boerlage and Broeze[8] had observed an inverse linear relationship between the octane number of a petrol and its cetene figure, whilst Dumanois[9] found that if a mixture of 15 per cent. of a Diesel fuel in a standard spirit is tested on the C.F.R. engine, a "heptane value" (reversed octane

[4] Le Mesurier and Stansfield, *J. Inst. Petr. Techn.*, 1931, **17**, 387.
[5] Le Mesurier and Stansfield, *N.E. Coast Inst. of Eng. and Shipb.*, 26.2.32.
[6] Boerlage and Broeze, *Engineering*, 1931, **132**, 603–606, 687–689; 755–756.
[7] Boerlage and Broeze, *S.A.E.J.*, 1932, **31**, 283.
[8] Boerlage and Broeze, *Proc. World Petr. Congr.*, 1933, **2**, 271.
[9] Dumanois, *Ann. des Comb. Liq.*, 1933, **8**, 490–492.

number) is found which correlates fairly well with the cetene number as determined on the Thomassen engine.

In the U.S.A.[10] the critical compression ratio (starting test) method with the C.F.R. engine, as devised by Pope and Murdock[11] would seem to find most favour. It is noteworthy that the results in this case are to some extent sensitive to engine conditions; Pope[12] has shown that two fuels which match each other in critical compression ratio under a certain set of conditions may no longer correspond if the temperatures and turbulence are altered. It still remains to be seen to what extent this sensitivity, which would imply a rigid standardization of engine test conditions, has a practical significance. Becker and Stacey,[13] who have also published data upon the above C.C.R. method, observed a very rough relationship between the C.C.R. and the aniline point of the fuel.

With regard to the use of the self-ignition temperature ("*e*"), the concensus of opinion seems to be that this method of judging Diesel fuel quality is very unreliable. The two last-named authors, however, found a fair correlation between the C.C.R. and S.I.T.'s observed in a Moore bomb.

Several authors have dealt with the fuels available for Diesel engine operation, or have devoted attention to methods of improving low-grade products. Interest in this matter is largely due to the fact that a Diesel fuel is almost exclusively a material obtained from overseas, for whilst petrol may be (and is) considerably supplemented by coal derivatives, it is not a simple matter to prepare a good fuel for C.I. engines from the same source.[14] The polymerisation of olefines for this purpose is theoretically (but at present not economically) possible, whilst the use of various animal and vegetable fats is attended by the disadvantages of their relatively low calorific value (due to their oxygen content) and of the difficulty of atomising them properly. Nevertheless, Schmidt[15] obtained fairly good results with pea-nut, soy-bean and palm oils, although trouble was experienced in starting. Gautier[16] reports satisfactory running on a slow-speed, large-bore engine (compression ratio 36) with palm oil, karite (shea) butter, pea-nut oil and castor oil. Several methods are mentioned for improving the

[10] For a review of the status in the U.S.A. see Schweitzer, Dickinson and Reed, *Proc. World Petr. Congr.*, 1933, **2**, 236.
[11] Pope and Murdock, *S.A.E.J.*, March, 1932.
[12] Pope, *Proc. World Petr. Congr.*, 1933, **2**, 266.
[13] Becker and Stacey, *Proc. World Petr. Congr.*, 1933, **2**, 262.
[14] Howes, *Proc. World Petr. Congr.*, 1933, **2**, 781.
[15] Schmidt, *Tropenpflanzer*, 1932, **35**, 386–389; *Chim. et Ind.*, **29**, 74; *Chem. Abstr.*, 1933, **27**, 1735.
[16] Gautier, *Rev. Comb. Liq.*, 1933, **11**, 18–24; *Chim. et Ind.*, **29**, 1320.

ignition quality of tar oils. Broche, Ehrmann and Scheer[17] state that they may be employed if the engine is supplied with a pre-chamber containing a catalyst such as an oxide of cerium, thorium or vanadium on asbestos wool. E.P. 395,601 (F. Krupp) deals further with the method previously reported for running a C.I. engine on a long-delay fuel, such as tar oil, consisting in the admission of a precharge of an easily ignitable oil. Johnson[18] has protected the addition to a Diesel fuel of a highly unsaturated compound such as diacetylene, or other liquid polymerisates from acetylene, and the use of a similar dope (including allylene, allene, butadiene, etc.) is the subject of a patent to the I.-G. Farbenindustrie.[19] The use of a mixture of medium or heavy hydrocarbons and 2–10 per cent. of ethyl alcohol is covered by another patent,[20] whilst Clerget[21] also advocates an addition of the latter substance.

Before leaving the subject of Diesel fuels, mention may be made of a paper by Bouman[22] on the formation of "lacquer" on the walls of the combustion space in C.I. engines. This deposit, which causes some trouble in practice when running at low loads, is a resinous body due to incomplete combustion. Some engines are in this respect sensitive to the cetene value of the fuel, which causes misfiring when idling.

Comparatively little has been published with regard to the use of gas or fuel oil for purposes other than for Diesel engines. The "refractory screen" oil-gas process,[23] in which fuel oil is sprayed on to a checker screen in a generator and oil is used for the heating-up period, has been described. Practical results with this process have been given by Wehrle.[24] An investigation into the composition of the tar obtained in the water-gas process when employing bunker enriching oil has been published by Griffin.[25] Several accounts have been given of results in American plants for the production of oil and carburetted water gas, partly intended as a stand-by in the event of an interruption in the local natural gas supply.[26,27,28,29]

[17] Broche, Ehrmann and Scheer, *Gas J.*, 1932, **200**, 490; *Gas u. Wasserfach*, 1933, **76**, 29–33; *Glückauf*, 1932, **68**, 965–982.

[18] E.P. 399,150.

[19] Fr.P. 746,116.

[20] Rutzebeck, E.P. 375,525.

[21] *Compt. rend.*, 1933, **196**, 1645–1647.

[22] Bouman, *Proc. World Petr. Congr.*, 1933, **2**, 248.

[23] Anon., *Chem. Met. Eng.*, 1932, **39**, 663.

[24] Wehrle, *Am. Gas J.*, 1933, **139**, No. 2, 7–9; *Chem. Abstr.*, **27**, 1933, 4904.

[25] Griffin, *Ind. Eng. Chem.*, 1933, **25**, 89.

Oils intended for gas-making purposes are frequently evaluated on a basis of their aromatic, naphthene and paraffin content. In order to test the accuracy of the method employed for distinguishing between the two last-mentioned groups of hydrocarbons, Griffith and Hollings[30] have prepared what they claim to be substantially pure paraffins and naphthenes from various gas oils, and with these materials have confirmed the assumption that 1 per cent. of "naphthenes" lowers the aniline point by 0·4° C. The authors see no reason for altering the conclusion of Griffith[31] to the effect that the therm yield in gas making is principally dependent on the sum of the paraffins and unsaturateds.

A laboratory investigation on the enrichment of water-gas with gas oils, published by Schläpfer and Schaffhauser,[32] deals with the effect upon the gas yield, etc., of varying temperature and rate of oil admission, and of the presence of hydrogen. The authors agree that the carburetting value of a gas oil, which depends on the boiling range and the chemical composition, may be expressed fairly well by the relationship proposed by Holmes,[33] but they prefer a new formula: $B=\frac{KH}{G}$ in which B is the carburetting value, H the hydrogen content of the oil, K the average boiling point (° C.) under 10 mm. pressure and G is the specific gravity. A good oil should have B=not less than 2600.

Some papers dealing with combustion calculation are of interest. Kilgore[34] has described the computation of a combustion chart suitable for most types of fuel, except producer and blast furnace gas, from the Orsat analysis of the flue gases. Burkhard[35] gives a formula (a modification of that presented by the U.S. Bureau of Mines) for calculating the amount of excess air required to burn a fuel which does not contain CO_2, CO, free O_2 or N_2. A paper by Nelson[36] draws attention to the misleading results which

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[26] Willien, *J. Western Soc. Engrs.*, 1932, **37**, 272–283; *Chem. Abstr.*, 1933, **27**, 179.

[27] Beard, *Am.Gas J.*, 1933, **138**, No. 6, 30–31; *Chem. Abstr.*, 1933, **27**, 4057.

[28] Nagler, *Am. Gas J.*, 1933, **138**, No. 6, 34; *Chem. Abstr.*, 1933, **27**, 4057.

[29] Pettyjohn, *Am. Gas Assoc. Monthly*, 1933, **15**, No. 8, 340–432; *Chem. Abstr.*, 1933, **27**, 4905.

[30] Griffith and Hollings, *J. Inst. Petr. Techn.*, 1933, **19**, 701.

[31] Griffith, *J.S.C.I.*, 1929, **48**, 252T.

[32] Schläpfer and Schaffhauser, *Gas J.*, 1933, **203**, 676.

[33] Holmes, *Ind. Eng. Chem.*, 1932, **24**, 325.

[34] Kilgore, *Petr. Eng.*, Nov., 1932, **4** (2), 88.

[35] Burkhard, *Petr. Eng.*, March, 1933, **4** (6), 62.

[36] Nelson, *Petr. Eng.*, Feb., 1933, **4** (5), 44.

are arrived at if the gross heat of combustion is used for refinery calculations instead of the net heat; the heating efficiency is discussed, and other data relative to fuel burner operation are given. Figlmüller[37] supplies equations for arriving at the percentages of CO_2 and CO in stack gases with complete and incomplete combustion, and for the percentage of O_2, from the specific gravity and the ratio of theoretical to actual amount of oxygen. A new formula: $Q = (3{\cdot}635H + 235{\cdot}9) \times \left(\frac{C}{3} + H - \frac{(O-S)}{8}\right)$ for calculating the calorific value from the elementary analysis is proposed by Grummel and Davis.[38]

The avoidance of the difficulties caused by the inhomogeneity of cracked residues has continued to receive attention. The Goodwin process, employing dilute sulphuric acid as a flocculating agent, was mentioned in last year's report. Haeck[39] has patented a process of homogenisation, consisting in a heat treatment at 70–100° for some hours, followed by an abrupt cooling of the surface, whereby a film is formed which precipitates and carries down solids with it. A patent to Carlyle[40] covers the cracking of an oil in the presence of lime, which facilitates the subsequent filtration of the carbonaceous matter. Another patent[41] deals with the use of a mixture of a solid adsorbent with a gas oil containing naphthenic acid, which is added to the fuel oil to be clarified. Filtration over carboniferous residues, such as those obtained in the hydrogenation of coal, tar, oil, etc., has been patented by the I. G. Farbenindustrie,[42] filtration through filter cloth covered with a material such as bleaching-clay, by the Bataafsche Petroleum Maatschappij.[43]

"Colloidal fuel," "coal-in-oil" or "disperse fuel" is apparently not out of the experimental stage yet, and is still the subject of a number of investigations. Manning[44] states that in order to obtain a stable suspension of pulverised coal with a particle size below 64 μ, it is necessary to increase the apparent viscosity of the fuel oil at low rates of shear—*i.e.*, to confer plastic properties to it. This may be done by means of very small amounts of soap—

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[37] Figlmüller, *Petr. Z.*, 1932, **28**, No. 47, 1–4.
[38] Grummel and Davis, *Fuel*, 1933, **12**, 199–203.
[39] Haeck, E.P. 389,925.
[40] Carlyle (to S.O.C. Ind.), U.S.P. 1,875,823.
[41] Swartz (Jenkins Petr. Co.), U.S.P. 1,878,650.
[42] Germ. P. 558,638.
[43] E.P. 387,896.
[44] Manning, *Proc. World Petr. Congr.*, 1933, **2**, 811.

e.g., 0·1–0·5 per cent. of sodium stearate. Schultes[45] described the results with colloidal fuel in an experimental plant arranged for the purpose in Bochum in 1932, using a suspension of coal dust in anthracene oil. According to Benthin[46] brown coal is particularly suitable for the preparation of disperse fuel, owing to the active character of the humic acids (ulmins) which it contains. Lignite creosote may be used for peptisation and small amounts of caustic alkali or pyridine may be added with advantage. The good points of colloidal fuel, more especially its high heat value per volume, is stressed by Tollemache.[47] Kern[48] has patented the preparation of a disperse fuel prepared with ground coal which has been plasticised with water or dilute HCl or $MgCl_2$ solution, rapidly heated to carbonisation temperature, cooled and pulverised, whilst French Patent 743,241[49] covers the addition to the oil used for suspension of gelatinising substances (such as paraffin, ceresin or ozocerite) and of substances (*e.g.*, vaseline, wool, fat, glycerides) which prevent hardening.

Finally, mention may be made of some articles dealing with the general and economic aspects of fuel oil use. The fact that, whilst gas or furnace oil is the base material par excellence for cracking, a considerable portion of the available product is employed for domestic heating, is stressed by Eckert and Pew,[50] who suggest that burners should be designed for cracked gas oils, in order to release as much as possible of the straight-run product. Russell and Hanks[51] discuss methods of dealing with, or preventing, a surplus production of fuel oil. The outlets which they believe capable of expansion are: its use as a substitute for coal, as a carburettant for water gas, as a material for the surface dressing of roads, and as a domestic fuel. They also discuss refinery operations (gasification, cracking, hydrogenation, etc.) which will result in the diminution of the fuel production. In a lecture delivered during the World Petroleum Congress, Kessler argued that the price-depression in the products of the petroleum industry (which is principally governed by the demand for gasoline) is mainly due to over-production of fuel oil, resulting in a trend to the "illegitimate" substitution of oil for other naturally indicated

[45] Schultes, *Proc. World Petr. Congr.*, 1933, **2**, 816; see also *Glückauf*, 1932, No. 52, 1198.

[46] Benthin, *Proc. World Petr. Congr.*, 1933, **2**, 813.

[47] Tollemache, *Colliery Guard.*, 1933, **146**, 569–571; *Iron and Coal Tr. Rev.*, 1933, **126**, 453–454.

[48] Kern, U.S.P. 1,899,811.

[49] To Radiochemisches Forschungsinstitut G.m.b.H.

[50] Eckert and Pew, *Oil & Gas J.*, 24.11.32, **31** (27), 27.

[51] Russell and Hanks, *Oil & Gas J.*, 1.12.32, **31** (28), 14.

fuels. A diminution of the fuel oil production, and a consequent revival of the industry, was stated to be best attainable by measures involving the removal of all straight-run fuel from the market, and by cracking this straight-run fuel according to existing methods.

Hutchinson and Breitenstein[52] have analysed the figures for the consumption of coal and petroleum fuel from 1850/1930, and prophesy that whilst the consumption of coal is not likely to increase much during the next 20 years, petroleum consumption will in all probability have doubled in the same period, assuming that sufficient low-priced reserves are available.

LABORATORY,
N. V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ.

[52] Hutchinson and Breitenstein, *Oil & Gas J.*, 23.3.33, **31** (40), 30.

Oil Engine Developments and the Testing of Diesel Fuels.

By R. Stansfield, A.M.Inst.C.E. (Member).

Engine development is continuing steadily towards the better use of airless injection systems, but there is still no indication whatever of any serious attempt on the part of builders to produce designs which will burn residual fuels or the heaviest of the distillates. On the contrary, the fuels demanded are almost exclusively the distillates, with a pronounced preference towards the narrower and lighter fractions. It is probable that a great part of the apparent improvement in engine behaviour recently is due more to a succession of small changes in fuels than to a marked advance in general design.

As regards injection systems, builders are turning more and more to proprietary pumps and injectors made by specialists. The manufacture of some of these has reached a very high standard of excellence, and there are many new makes awaiting or undergoing trials under service conditions.

There is no tendency towards an increase in the number of designs of engine using open type spray valves, the spring loaded needle valve being almost universal.

Among recent engine developments the following are of special interest :—

The Doxford opposed piston two-stroke engine has been redesigned with welded frames, and the modifications have resulted in a considerable saving of both weight and space, although the general rigidity has been increased. A fuel consumption of 0·355 lb. per s.h.p. hour has been obtained on an engine of this type developing 3200 h.p. in four cylinders at 95 r.p.m.

The Scott engine has been further developed, also with notable saving in space, both in respect of length and head room. Reduction of head room in this instance has been effected by using a rotary valve in the exhaust outlets, and this has made it possible to shorten the piston skirts considerably.

The Richardson Westgarth marine engine has been improved both as regards space occupied, weight per horse power, and the design of the cylinder and scavenging system in such a way as to improve combustion and reduce fuel consumption.

Both Crossley's and the Brush Electrical Engineering Company have introduced enclosed horizontal engines. The latter range includes an interesting four cylinder design, with two pairs of horizontally opposed four-stroke cylinders operating on two cranks.

The use of supercharging at low pressures is increasing, and is included in the engines made by Vickers-Armstrong for the submarine *Thames*, and in the "Sirron" engine built by the Newbury Diesel Company for small coasting vessels.

The application of the Diesel engine to locomotive work is increasing rapidly. Changes are being made in the older designs of engine better to adapt them to this duty, and engines are being fitted which have not hitherto been associated with this class of vehicle.

A good idea of the progress made is obtainable from the output of Armstrong Whitworth's during 1933. This included a lightweight railbus for fast branch line service; a light motor train of the Diesel-electric type fitted with a 500 b.h.p. engine and drawing three coaches; a main line locomotive of 1700 b.h.p.; a design with an engine of 880 b.h.p.; shunting locomotives; and a 95 b.h.p. engined oil-electric tractor locomotive operating a narrow-gauge train, the engine in this case being of the Armstrong-Saurer type.

Road vehicles are still steadily increasing in numbers, and some of the well-known builders have made important improvements in their designs. The Armstrong-Saurer type has been redesigned as regards the combustion space, the spray valve position and the air cell and throat having been radically altered to give an improved performance. A new design of the MacLaren Benz engine has been introduced, with a further addition to the many existing types of combustion chamber.

In general the design of high speed engines has been mainly towards detail alteration to secure greater reliability, especially as regards bearings and cylinder life. Dilution of the lubricating oil, once noticeable on certain engines, has practically disappeared.

Attempts are being made to increase the maximum speed which can be reached before smoke becomes objectionable. The Perkins engine, with a novel form of air cell and with injection from the throat both into the main cylinder and into the cell, has been run up to 4000 r.p.m. in the case of the 2·2 litre, four cylinder size. This is the maximum speed and above the smoke point when the full load is being carried, but the exhaust clears with a moderate easing of the load and is not noticeable under ordinary driving conditions. The cost of the fuel pumps and spray valves is still an important factor in the high initial cost of the high speed engine for road vehicles, but attempts are being made to produce the remaining details of certain makes on a production basis more in line with the manufacture of petrol engines.

There is still no indication of any tendency to develop mainly either the direct injection or the air cell type of engine, each having

its special advantages. The fuel consumption of the former seems, however, to be superior to that of its rivals.

Developments in methods of testing fuels for compression ignition engines have been mainly detail improvements in apparatus. Running tests in slow and high speed engines, critical compression ratio tests in variable compression engines, throttling tests in conjunction with indicator diagrams for delay determination, and throttling tests at a fixed compression ratio to determine the degree of throttling at which misfiring occurs have all been explored, and details of the results were given in several papers read before the World Petroleum Congress in July, 1933.

It is generally agreed that the ignition quality of a fuel is one of the most important characteristics to be determined, but a considerable degree of caution is being observed to avoid premature standardisation of any special method of test at a time when engine design, particularly in the case of high speed engines, is by no means fixed.

Running tests have shown that there is not a large difference between the relative ignition qualities of a series of fuels when they are tested in several types of compression ignition engine, provided low compression ratio designs which rely on hot spots for heating the air charge locally to the necessary temperature are omitted. There are, however, a few exceptional types of fuel such that a change from one design of engine to another might lead to a difference in relative ignition quality rating and give rise to comment from the user. The position will probably develop along the same lines as that for the testing of gasolines—*i.e.*, a method will be used which is found to give agreement with an average of road and other service tests. In view of changes in engine design and possible extension of sources of fuel supplies for high speed engines it would, obviously, be unwise to force standardization of a test method at present.

There is no general agreement regarding the terms in which ignition quality should be expressed, but it was recommended at the World Petroleum Congress that any method suitable to the test conditions should be used, and, when possible, the cetene number should be given as well. The cetene number of a fuel is now defined as the percentage by volume of a blend of cetene and α-methyl-naphthalene which has the same ignition quality as the sample under test and when tested under the same conditions.

Some doubt regarding the stability of available supplies of cetene (which is not readily obtainable in a pure condition) has been expressed both in America and here, results on tests of fuel samples having shown differences between one laboratory and

another only attributable to change in the cetene component of the standard blends.

There is also lack of unanimity of opinion regarding the effect of change of engine conditions on relative ratings of fuels, but the tests which show the greatest changes seem to be those which least repeat running conditions. The most definite alterations in rating, especially when starting quality is compared with running quality, are those which occur with doped fuels.

Apart from these exceptions, the use of a test which depends on motoring the engine and finding the compression ratio or the degree of throttling at which firing is only just possible has much to recommend it on account of its simplicity and the absence of expensive apparatus. If means are available for making tests at two different temperatures, then an abnormal fuel sample may be detected by the alteration in rating from one temperature to the other, and neither test will accurately indicate the running quality. This defect of the motoring test may not, however, be important, since temperature sensitive fuels require a final test in the actual engines in which they are to be used.

Among the methods of test which are described in detail are the following :—

Throttling tests on the Thomassen engine which runs at a slow speed, and for which a high speed pencil type indicator is used to obtain a superimposed series of diagrams during progressive throttling of the inlet air. The curve drawn through the points of break away of the combustion lines from the compression lines enables the delay angle at a given pressure to be measured with reasonable accuracy, and results are converted to cetene numbers by means of comparative tests against suitable calibrated secondary standards.

A second method of test, developed in the laboratory responsible for the throttling test with the Thomassen engine, depends on the use of a modified C.F.R. engine, which has an air cell and a cool connecting throat to the main cylinder. The air cell is cylindrical in section and one of the ends can be adjusted to control the compression ratio. Fuel quality is measured by matching against calibrated secondary standard blends, and either a modified bouncing pin or an optical method is applied to determine the knock intensity or the end of the delay period.

A further method, which is useful in laboratories where only the standard C.F.R. engine is available, is to determine the octane number of a blend of the sample and a specified gasoline, high cetene number Diesel fuels having the greatest pro-knock effect when blended and tested in this way.

The American modification of the C.F.R. engine to a Diesel engine has been used to determine the critical compression ratio below which firing does not take place in a motored engine, and the same engine has also been used with less satisfactory results for running tests.

Among the more indirect tests are the Moore bomb test and the aniline point determination. Although some workers still seem to consider that the former gives reasonable correlation with engine results, general opinion, based on actual tests, is against this view. As regards the aniline point test, it is not claimed that this gives exact agreement with engine ratings, but it is a useful preliminary and simple method for ascertaining whether any unknown sample is likely to be good or bad.

For detailed information regarding the various methods of test referred to above, the papers read on this subject at the World Petroleum Congress, Vol. 2 or Sectional Volume E, should be consulted.

Asphalts and Road Materials.

By J. Greutert and R. J. Forbes.

General.

Statistics relating to world trade in, and the production of asphaltic bitumen in the years 1930 and 1931 form the basis of an article by W. Schmidt.[1] A special survey of the importance of asphaltic bitumen to German industry was drawn up by Heinrici.[2] At the time when this survey was made no particulars regarding the production and applications of asphaltic bitumen in America had yet been published.

Chemical.

An important point of investigation last year was the paraffin wax content of asphaltic bitumens. It is contended in an article by Müller and Wandycz[3] that paraffin wax in soft asphaltic bitumens may have a bad effect, while in hard asphaltic bitumens it may have a good effect upon the ductility. By the judicious choice of the mode of distillation the influence of the paraffin wax can be steered into the right channels. In connection with this problem, Fussteig's[4] solution is also worthy of note. This author suggests that the paraffin wax should be removed by cracking and the asphaltic bitumen then freed from coke by one of the two processes he proposes. Adel[5] considers paraffin wax in quantities up to 4 per cent. to be inoccuous, but recommends 2·5 per cent. as the maximum in asphaltic bitumens for road-making purposes. (Also see Riehm, *World Petr. Congr.*, Paper No. 46.)

Tietze came to the conclusion that undue value should not be attached to the micron content of tar when judging its utility.[6]

Rick[7] investigated the weathering of asphaltic paints and compositions not exposed to the light.

Interesting particulars regarding the influence of tropical climate upon thin layers of petroleum asphalt are brought to light in de Kraeff's publication.[8] It emerges that the changes in melting point and penetration are far more marked than those in ductility or carbene content.

W. Maass indicated a number of improved methods for the determination of various components of asphaltic bitumen (Hartasphalte, Weichasphalte, Asphaltharze, Oelige Anteile, Paraffin) and by

[1] *Petroleum*, 1933, **50**, 12.
[2] *Bitumen*, 1933, **7**, 142.
[3] *Asphalt u. Teer*, 1933, **25**, 421.
[4] *Teer u. Bitumen*, 1933, **16**, 191.
[5] *Asphalti, Bitumi, Catrami*, Nov., 1932.
[6] *Asphalt u. Teer*, 1933, **39**, 718.
[7] *Asphalt u. Teer*, 1933, **30**, 517.
[8] N.I.W.V. Publ., No. 123.

these methods examined a large number of bitumens of different origin. He also devoted special attention to the course of the oxidation as dependent upon the paraffin wax present.[9]

Physical Properties.

The changing of tar in road carpets through overheating while being laid forms the subject of a study by Bierhalter,[10] who also suggests a method by which this overheating can be detected.

Signs of ageing in tar also induced Neumann[11] to stress the necessity for strict supervision during the production of tar so that a more uniform product should be obtained.

Barr[12] and Westmeyer,[13] among others, give comparative charts of viscosities measured with different instruments.

Eymann[14] discusses in broad outline the problem of the viscosities of asphaltic bitumens, tars or mixtures of the two. A searching study of the instruments used to measure kinematic viscosities is made by Garner and Kelly.[15]

Obst[16] shows how great is the influence of micro-asbestos upon the elastic properties of asphalt compositions.

A problem which is gaining in prominence is the adhesion of layers of asphaltic bitumen or tar to mineral aggregate as used in road making. The theoretical side of this problem was elucidated in various publications by, *inter alia*, Saal[17] and Kindscher.[18] An important series of experiments relating to this adhesion of bitumens to minerals was carried out by Riedel and Weber[19] who, after examining a series of minerals, asphaltic bitumens and tars, came to the conclusion that the decisive factor in this adhesive power is the properties of the minerals.

The problem of tar-bitumen mixtures and the stabilisation of these mixtures also enjoyed general attention. Macht[20] gave a survey of the present stage of this problem. Rashkovich[21] argues in favour of the use of natural asphalts in his article, "Les Mélanges Goudron-Bitume," in order to obtain more stable mixtures. Such mixtures are even recommended as emulsion.[22]

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[9] *Proc. World Petr. Congr.*, 1933, **2**, 557.
[10] *Asphalt u. Teer*, 1933, **34**, 599.
[11] "Stufa Teerauschuss," Nürnberg, 1933, p. 39.
[12] *Roads and Road Constr.*, 1933, **127**, 221.
[13] *Mitt. Teerstrassenbau Essen*, 1933, **3**, 24.
[14] *Teer u. Bitumen*, 1933, **14**, 166.
[15] *Physics*, 1933, **4**, 97.
[16] *Teer u. Bitumen*, 1933, **3**, 30.
[17] *Bitumen*, 1933, **5**, 101.
[18] *Bitumen*, 1933, **5**, 104.
[19] *Asphalt u. Teer*, 1933, **37**, 677.
[20] *Proc. World Petr. Congr.*, 1933, **2**, 581.
[21] Deux. Congrès Belge Anvers, 1933.
[22] *Wasser u. Wegebau Z.*, 1933, **15**, 179.

Rock Asphalts and Natural Asphalts.

A large number of sources of asphaltic rock in France are mentioned in *Chimie et Industrie* (1933, No. 4, page 124T). A number of new sources of such rock in Siberia also became known.[23]

The winning and purifying of natural asphalts, generally, forms the subject of an article in the *Engineer* (1933, Vol. 155, No. 4029, page 326). The Italian Government is particularly interested in these asphalts, notably in connection with its plans for the building of motor roads in that country. See, *inter alia*, articles in *Annali dei Lavori Pubblici*, 1932, pp. 8–36, and in *Le Strade*, 1933, No. 2.

On account of the large quantities of petroleum asphalt imported into Germany, the question as to whether and to what extent German natural asphalts could be substituted for part of this imported material has recently been repeatedly investigated by Steinke[24] and Moll,[25] among others.

Petroleum Bitumen.

General.—Many articles deal with bitumens and their uses in a general sense. For lack of space, we shall here mention only the most important; thus, by Spielmann,[26] Obst[27] regarding asphaltic bitumens, tars and mixtures of these. In a long article, Fischer supplies important particulars relating to various industrial tar pitches and grease pitches[28]; Boulard furnishes a general article on asphaltic bitumen.[33] Cutbacks which, in recent years, have been coming into more and more prominence in road making, are dealt with in detail by Prév. Hubbard, not only as to their properties and uses, but also as to the methods of testing them.[29] An article by Pagès and Houlnick,[30] which discusses the newer American and German literature, is of similar purport.

In his "Tätigkeitsbericht," P. Herrmann criticises the methods of examining cutbacks as formulated in the German standards,[31] while von Skopnik fully explains the relation between these standards and practical requirements.[32] In the course of last year G. H. Klinkmann's dissertation on tar-bitumen mixtures (*Allg. Industrie-Verlag*, Berlin) was published.

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[23] *Petr. Times*, 1933, **29**, 401.
[24] *Wasser u. Wegebau Z.* 1933, **8**, 89.
[25] *Strassenbau*, 1933, **19**, 242.
[26] *Roads and Road Constr.*, 1933, **128**, 245.
[27] *Teer u. Bitumen*, 1933, **7**, 82.
[28] *Teer u. Bitumen*, 1933, **24**, 285.
[29] *Roads and Streets*, 1933, **1**, 19.
[30] *Revue Gén. des Routes*, 1933, **86**, 49.
[31] *Asphalt u. Teer*, 1933, **21**, 356.
[32] *Teer u. Bitumen*, 1933, **15**, 177.

Nomenclature and Specifications.—Unfortunately, the nomenclature of bitumens, a problem of international importance,[33] is no nearer solution. This is clearly evident from a survey written by R. Schwarz.[34]

The new "Zentralstelle für Asphalt und Teerforschung" in Germany supplies a new classification for the Reichspatent-register, and this classification is discussed in several quarters.[35,36]

In his "Tätigkeitsbericht, 1931,"[37] P. Herrmann gives clear definitions for various forms of cold asphaltic bitumen or tar.

A large number of specification for asphaltic bitumen for various uses were published last year.

Westmeyer and von Skopnik deal fully with the new German standards for asphaltic bitumen, tar, cutbacks and emulsions for road making.[38] Mallisson[39] discusses the German standards for pointing mastics. The "Stufa" issued a new "Merkblatt" indicating the most highly recommended tar road carpets.[40]

The Austrian road construction standards are the subject of an article by Ettel,[41] while A. de Renzo[42] discusses the claims made upon road building materials by the city of Milan.

Nellensteyn goes fully into the new specifications issued by the Rijkswaterstaat for road making, 1933,[43] at the same time describing those methods of investigation which are not included in the "K.V.B.B., 1930." Nellensteyn also discusses[44] the testing of, and specifications for, tar-coated stone and tar-coated slag in Holland.

The French specifications for asphaltic road carpets are dealt with in an anonymous article in *Verkehrstechnik*,[45] while Marcotte deals specially with the specifications for tar in the light of the difficulties which the French tar industry had to overcome in order to be able to meet these specifications.[46]

Finally, Batta compares the Belgian specifications for road tars with those of some other countries.[47]

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[33] "Revue Pétrolifère," 1933, p. 338.
[34] *Petroleum*, 1933, **29**, Mitt. I.P.K., 1–4.
[35] *Asphalt u. Teer*, 1933, **20**, 341.
[36] *Asphalt u. Teer*, 1933, **21**, 355.
[37] *Asphalt u. Teer*, 1933, **22**, 374.
[38] *Verkehrstechnik*, 1933, **6**, 155.
[39] *Asphalt u. Teer*, 1933, **42**, 555.
[40] *Teer u. Bitumen*, 1933, **11**, 139.
[41] *Strassenwesen*, 1933, **3**.
[42] *Le Strade*, 1933, **1**.
[43] *Wegen*, 1933, **7**, 183.
[44] *Wegen*, 1933, **17**, 501.
[45] *Verkehrstechnik*, 1933, **11**, 291.
[46] *Revue Gén. des Routes*, 1933, **91**, 246.
[47] Deux. Congrès Belge Anvers, 1933, No. A.VIII.

Application.

Road Building.—In view of the financial crisis, an article by Oberbach, surveying the economical value of various bituminous road carpets,[48] is important. In Dutch periodicals some interesting articles appeared, written by various Directors of Municipal Works, each describing his local experience of bituminous road carpets during the last decade, notably Mr. Clerx for Amsterdam[49] and Mr. Dekker for The Hague.[50]

In connection with the extensive plans for the laying of motor roads in Germany, Becker[51] points out the advantages of bituminous road carpets, while Eichler considers these carpets from the point of view of the road user.[52] Hughes[53] goes fully into the problems of bituminous surface dressing, while Claes[54] explains the advantages of this process of road making for the upkeep of concrete roads. A number of road tests were made in the Dutch Indies to try out the utility of Boeton natural asphalt for the surface dressing of macadam roads.[55] Some articles on tar for road-making purposes were published by Grossjohann[56] and S., the latter's article containing some important statistics.[57] Bauerfeld drew special attention to the present-day method of testing road tar, and to the ideal specifications and methods of test which it will be necessary to strive to attain if the tar problems in road making are to be solved.[58] In connection with this article there is an important paper by Luer, who compares the investigations made by official authorities in England and Germany.[59]

The use of cutbacks in road making was a problem treated from very different angles. The American points of view, also regarding the claims to be made upon cutbacks, were thoroughly gone into by Prév. Hubbard.[60] These forms of construction were introduced into Italy by an article published by Becker.[61] Friedel[62] cites a few examples of the use of cutbacks in Austria. P. Herrmann instituted an interesting investigation into the sensitiveness to

[48] *Bitumen*, 1933, **2**, 25.
[49] *Wegen*, 1933, p. 346.
[50] *Wegen*, 1933, p. 277.
[51] *Asphalt u. Teer*, 1933, **35**, 620.
[52] *Bitumen*, 1933, **7**, 147.
[53] *Surveyor*, 1933, **3**.
[54] Deux. Congrès Belge Anvers, 1933, Sect. A.IV.
[55] N.I.W.V. Publ., No. 121.
[56] *Teer u. Bitumen*, 1933, **7**, 73.
[57] *Teer u. Bitumen*, 1933, **12**, 144.
[58] *Asphalt u. Teer*, 1933, **24**, 405.
[59] "Teerauschuss der Stufa," Nürnberg, 1933, p. 13.
[60] *Roads and Streets*, Feb., 1933.
[61] *Asfalti, Bitumi, Catrami*, 1933, **2** and **3**.
[62] *Strassenwesen*, 1933, **2**.

water of rock asphalt, which disclosed the fact that the mineral aggregate is chiefly responsible for this phenomenon.[63]

Blocks of asphalt were tested in Alkmaar (Holland) and there proved to be satisfactory.[64]

The latest progress in the construction of rolled asphaltic roads in Germany were discussed by Neumann[65] with reference to the most recent literature on the subject. Kerkhof collected the latest Dutch data[66] on the same subject, while Holoffe discusses the experience of Belgian road engineers.[67] An important contribution as regards the composition of these closed road carpet mixes is Chevallier's study of the changes in the properties of bitumens brought about by the addition of fillers.[68]

The cold-applied mixes of this closed type formed the subject of extensive research made by Temme.[69]

The examination of samples taken from old asphaltic macadam roads revealed the fact that this type keeps in good condition. Ohse[70] found that the extracted bitumen still "conforms to all reasonable demands." The advantages of what is known as "Cold Asphalt Macadam" were explained by Wace.[71]

According to Temme, very good results were obtained in Germany East Prussia—with asphalt macadam roads.[72] Martin[73] went thoroughly into the use of cutbacks for carpets of that kind.

For lack of practical experience, the advantages or disadvantages of tar-bitumen mixtures for road making are not yet sufficiently known. For this reason, articles by Oberbach[74] and Schläpfer[75] on this subject are of interest.

According to Lenck, tar macadam roads appear to be satisfactory in Germany[76]; Heicken gives full details regarding the experience in Bavaria with this system.[77] Tar cutbacks have also been given a trial in recent years; Ertle surveys the results hitherto obtained which, for road mix carpets, still leave much to be desired.[78] A long article by Neumann[79] deals with the correct

[63] *Asphalt u. Teer*, 1933, **14**, 233.
[64] *Wegen*, 1933, **13**, 381.
[65] *Teer u. Bitumen*, 1933, **30**, 357.
[66] *Bitumen*, 1933, **3**, 41.
[67] Deux. Congrès Belge Anvers, 1933, Sect. A.III.
[68] *Science et Industrie*, 1933, No. La Route, 86.
[69] *Bitumen*, 1933, **3**, 60.
[70] *Teer u. Bitumen*, 1933, **9**, 105.
[71] *Roads and Road Constr.*, 1933, **124**, 115.
[72] *Bitumen*, 1933, **4**, 72.
[73] *Bitumen*, 1933, **2**, 31.
[74] *Teer u. Bitumen*, 1933, **18**, 213.
[75] *Schweiz. Z. f. Strassenwesen*, 1933, **17**, 169.
[76] *Wasser u. Wegebau*, 1933, **1**, 6.
[77] "Teerausschuss Stufa," Nürnberg, 1933, p. 53.
[78] "Teerausschuss Stufa," Nürnberg, 1933, p. 74.
[79] *Asphalt u. Teer*, 1933, **4**, 51.

composition of tar concrete mixtures. Laeger compares the tar concrete used in practice in England with that used in Germany, and also records the changes in composition which took place after laying.[80]

Leipold[81] argues in favour of the use of bitumen-impregnated sandstone, while the use of tar and/or asphaltic bitumen-containing cement in road making, etc., latterly is discussed in various quarters; thus by Biehl[82] and Orthaus.[83]

Holland's experience in surface dressing with asphaltic bitumen, cutbacks and emulsions is summarised in an article by Kryn.[84] England's findings in this regard are dealt with by Attwool.[85] Léauté[86] published the results of his investigation of the signs of the ageing of bitumens in the surface film.

The Bureau of Public Roads carefully examined the practical value of tar for surface dressing and for mix-in-place work.[87] Klein published a number of articles on surface dressing with tar.[88]

Miscellaneous Industrial Applications.—In the past year the use of bituminous material for the protection of dykes and banks and other hydraulic engineering purposes has come into particular prominence. An extensive report on experiments by Möszlang[89] is of interest in this respect. There were also numerous publications of this type on the waterproofing of bridge carpets, buildings, etc. Of these, special mention may be made of Greger's articles, [90,91] and Rick's[92] particularly on building materials; then papers by Schuster[93] and Rohde,[98] especially on bridge carpets.

With regard to asphaltic paints, von Hortenau investigated their brittleness and adhesion.[94] A survey by Obst[95] deserves special mention, while Gerlach carefully considers the anti-corrosive properties of bituminous paints.[96]

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[80] *Teer u. Bitumen*, 1933, **26**, 312.
[81] *Verkehrstechnik*, 1933, **19**, 493.
[82] *Wasser u. Wegebau Z.*, 1933, **18**, 212.
[83] *Wasser u. Wegebau Z.*, 1933, **11**, 130.
[84] *Wegen*, 1933, **10**, 289.
[85] *Roads and Road Constr.*, 1933, **121**, 13.
[86] *Science et Industrie*, 1933, No. La Route, 76.
[87] *Public Roads*, Vol. 14, No. 1.
[88] *Asphalt u. Teer*, 1933, **35**, 624.
[89] Mitt. No. 2, *Forsch. Instit. für Wasserbau u. Wasserkraft.*
[90] *Bitumen*, 1933, **2**, 38.
[91] *Bitumen*, 1933, **27**, 321.
[92] *Bitumen*, 1933, **6**, 118.
[93] *Asphalt u. Teer*, 1933, **13**, 219.
[94] *Farbenchemiker*, 1933, **4**, 127.
[95] *Teer u. Bitumen*, 1933, **8**, 82.
[96] *Bitumen*, 1933, **3**, 52.

Mallison[97] discussed the corrosive influence of roofing paper containing tar upon roof zinc, while Schwaderer[100] throws some light on the upkeep of roofing paper coverings. Rick studied the ageing of plastic bituminous masses.[99]

Emulsions.—Hixton and Fain published some of their observations relative to the stabilisation of asphalt emulsions.[101] An important study made by Bechler[102] deals with the "breaking" and "stabilisation" of emulsions, until he ultimately arrives at the determination of a "Zerfallswert" (dissociation value) which, he claims, provides better characterisation of emulsions than existing methods do. There is an article of the same category[103] by Weber, in which he specially studies the breaking and final setting of emulsions in relation to the various stones, which are generally the determining factor. This theory is repeatedly expounded in further articles by Weber[104] and Walther,[105] while Bierhalter[106] approaches the problem from another angle. Meanwhile, neither Suida nor Ueberreiter[107] have so far obtained concordant results with the "Zerfallswert" determination and press for a further description of various details of procedure. Klinkmann[116] published this method in the Italian technical press. Clayton deals with several general problems of road emulsions,[108] while von Skopnik points out the possibility of using German natural asphalt in the form of emulsion for road making.[109]

The latest advances in road emulsions, like emulsions for coating chippings, emulsions which hold coarse chippings, etc., are discussed by Geissler,[110] who would like to classify the emulsions in certain groups. In an article of similar purport Caroselli[111] proves to disagree with this grouping. Ellert deals with the good results obtained with road carpets consisting of road mixes incorporating emulsion ("Goudex") in Denmark.[112]

Finally, several publications by American authors saw the light

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[97] *Teer u. Bitumen*, 1933, **29**, 345.
[98] *Wasser u. Wegebau Z.*, 1933, **7**, 80.
[99] *Teer u. Bitumen*, 1933, **22**, 263.
[100] "Bautenschutz," 1933, p. 130.
[101] *Ind. Eng. Chem.*, 1932, **24**, 1336.
[102] *Teer u. Bitumen*, 1933, **21**, 249.
[103] *Teer u. Bitumen*, 1933, **28**, 333.
[104] *Asphalt u. Teer*, 1933, **8**, 144.
[105] *Asphalt u. Teer*, 1933, **38**, 698.
[106] *Asphalt u. Teer*, 1933, **31**, 539.
[107] *Petroleum*, 1933, **29**, 1.
[108] "Quarry and Roadmaking," 1933, p. 433.
[109] *Asphalt u. Teer*, 1933, **32**, 557.
[110] *Asphalt u. Teer*, 1933, **34**, 593.
[111] *Teer u. Bitumen*, 1933, **33**, 398.
[112] *Wegen*, 1933, **7**, 190.

on "Low Cost Roads" with bituminous emulsions, including those by Shaw,[113] and McKesson, Ostrander and Kern.[114]

Bierhalter[115] draws attention to the utility of emulsions for the application of protective coatings to buildings.

Temme[117] furnishes an elaborate survey of the methods employed by different countries for the testing of emulsions, while an article of similar purport was published by Wagner.[118]

An important article by Riis[119] deals with the specifications and research methods applicable to emulsions in Denmark. Two separate attempts were made at the World Petroleum Congress to arrive at international specifications and tests for roadmaking emulsions, viz., by the Syndicat des Fabricants d'Emulsions Routières de Bitume[120] and by the Technical Committee of the Road Emulsion and Cold Bituminous Roads Association.[121]

Testing.—Eymann[122] referred to the difficulties caused by the naphthalene content of tar when determining their viscosity.

Basler and Miegl reported on their experiments aiming at differentiating between various bitumens by the figures representing the spread of solutions of bitumens in CS_2+ petroleum ether on filter paper.[123]

Greutert published new methods for the determination of the flow of asphaltic bitumens, of the sagging of asphalt compositions under pressure and of the adhesion of cable fillers.[124] Herrmann suggested a new method for the determination of bituminous mastics' resistance to impact.[125]

Regarding the recovery of asphaltic bitumen from bituminous road carpets, articles were published by Kraëff[126] and Moll,[127] the latter also discussing determinations for percentage of binder and void.

Wilson described a rapid analysis for asphaltic bitumen *ex* road carpets by extraction with trichloroethylene and a special, rapid-working filter.[128]

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[113] *American City*, 1933, **3**.
[114] *Public Works*, 1933, **1**.
[115] *Asphalt u. Teer*, 1933, **36**, 661.
[116] *Asphalti, Bitumi, Catrami*, 1933, **3**.
[117] *Asphalt u. Teer*, 1933, **27**, 457.
[118] *Z. f. Angew. Ch.*, 1933, **46**, 263.
[119] *Proc. World Petr. Congr.*, 1933, **2**, 630.
[120] *Proc. World Petr. Congr.*, 1933, **2**, 644.
[121] *Proc. World Petr. Congr.*, 1933, **2**, 674.
[122] *Teer u. Bitumen*, 1933, **27**, 325.
[123] *Koll. Zeitschr.*, Bd. LIX., Heft 3, 345.
[124] *Bitumen*, 1933, **6**, 124.
[125] *Asphalt u. Teer*, 1933, **23**, 411.
[126] *Wegen*, 1933, **22**, 649.
[127] *Teer u. Bitumen*, 1933, **17**, 201.
[128] *Roads and Road Constr.*, 1933, No. 128, 256.

The analysis of road carpets generally was the subject of an article by Neumann[129] and von Skopnik.[130] Wilson[131] expatiated on the mechanical testing of bituminous mixtures, and particularly the stability, impact and tensile tests, while Adam and Murdoch published valuable figures relating to the same subject.[132]

Treating of the examination of tar road carpets, Hoepfner described methods for the analysis of the tar-bitumen mixtures used and the degree to which the tar resinifies[133]; the latter determination evoked a controversy with Herrmann.[134]

With regard to the analysis of tar-bitumen mixtures, Le Gavrian[135] published some views regarding the modified Mallison method, Nellensteyn[136] published his new method, while Mallison compared the two.[137]

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[129] Public Works, Roads and Transport Congr., 1933, Paper No. 20.
[130] *Bitumen*, 1933, Heft 1, 21.
[131] *Chemistry and Industry*, Vol. 51, No. 4.
[132] Public Works, Roads and Transport Congr., 1933, Paper No. 4.
[133] *Asphalt u. Teer*, 1933, **12**, 199.
[134] *Asphalt u. Teer*, 1933, **27**, 462.
[135] *Proc. World Petr. Congr.*, 1933, **2**, 580.
[136] *Proc. World Petr. Congr.*, 1933, **2**, 577.
[137] *Proc. World Petr. Congr.*, 1933, **2**, 573.